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ENVIRONMENTAL FATE STUDIES ON CERTAIN MUNITION WASTEWATER CONSTITUENTS

Final Report, Phase I — Literature Review

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March 1980

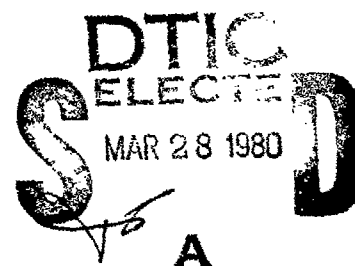
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The objective of this study was to perform a literature review on the trans- port and transformation processes that may affect the environmental fate of 11 munition wastewater constituents. Estimates of kinetic rate constants for vol- atilization, sediment adsorption, biodegradation, photolysis, chemical oxidation were made from available literature data. Recommendations for the further elucidation of environmental fate are made to fill the gaps identified in the literature review.			

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GLOSSARY OF TERMS

k_v^C	- Mass transport coefficient constant for compound
k_g^W	- Mass transport coefficient constant for water
k_v^C/k_g^W	- Mass transport coefficient ratio for compound
K_{oc}	- Sorption partition coefficient based on organic carbon content
H_c	- Henry's Law constant
k_A	- Hydrolysis rate constant under acidic conditions
k_N	- Hydrolysis rate constant under neutral conditions
k_B	- Hydrolysis rate constant under basic conditions
k_h	- Hydrolysis rate constant
k_p	- Photolysis rate constant
K_{OH}	- Equilibrium constant for the addition of OH^-
P	- Vapor pressure
K_p	- Sediment sorption partition coefficient
F_{OC}	- Sediment organic carbon content
nm	- Nanometers
cm	- Centimeters
λ_{max}	- Absorption wavelength maxima
UV	- Ultra-violet
ppm	- Parts-per-million
g	- Grams
ml	- Milliliters
K_{eq}	- Equilibrium constant

- K_a - Dissociation constant
- k_{ox} - Chemical oxidation rate constant
- M^w - Molecular weight of water
- M^c - Molecular weight of chemical
- L - Depth of water body

CHEMICAL ABBREVIATIONS

TNT	- 2,4,6-Trinitrotoluene
1,3,5-TNB	- 1,3,5-Trinitrobenzene
TNBAL	- 2,4,6-Trinitrobenzaldehyde
4-Az	- 2,2',6,6'-Tetranitro-4-azoxytoluene
6-Az	- 2,2',4,4'-Tetranitro-6-azoxytoluene
2-A-4,5-DNT	- 2-Amino-4,5-dinitrotoluene
4-OHA-2,6-DNT	- 4-Hydroxylamino-2,6-dinitrotoluene
4-A-2,6-DNT	- 4-Amino-2,6-dinitrotoluene
RDX	- 1,3,5-Trinitrohexahydro-1,3,5-triazine
TNG	- Trinitroglycerine
2,4-DNT	- 2,4-Dinitrotoluene
2-A-4-NT	- 2-Amino-4-nitrotoluene
4-A-2-NT	- 4-Amino-2-nitrotoluene
1,3-DNB	- 1,3-Dinitrobenzene
2,6-DNT	- 2,6-Dinitrotoluene
2,3,6-TNT	- 2,3,6-Trinitrotoluene
2-A-4,6-DNT	- 2-Amino-4,6-dinitrotoluene
3,4-DNT	- 3,4-Dinitrotoluene
5-A-2,4-DNT	- 5-Amino-2,4-dinitrotoluene

SUMMARY

The purpose of this phase of the project was to review the literature to identify and estimate the magnitude of the transport and transformation processes believed to be important in describing the environmental fate of 11 munition wastewater constituents in the aquatic environment. These constituents were 2,4,6-TNT; RDX; 2,4-DNT; TNG; 1,3-dinitrobenzene; 2,6-DNT; 1,3,5-trinitrobenzene; 2,3,6-TNT; 2-amino-4,6-dinitrotoluene; 5-amino-2,4-dinitrotoluene; and 3,4-DNT.

The literature was surveyed to obtain rate data pertaining to the photolysis, hydrolysis, oxidation, reduction, microbial transformation, volatilization and sediment sorption processes for each compound. Physical (solubility and vapor pressure) properties were also investigated to aid in the estimation of process rates.

The results of this review indicate there is little information available for determining the environmental fate of the subject compounds. Although many fate processes were identified for each compound, the available kinetic rate estimates could not be extrapolated to environmental conditions.

The processes believed to be dominant fate processes were identified, and recommendations for the necessary studies to fill the gaps in the literature for each compound were made.

INTRODUCTION

The U.S. Army Medical Bioengineering Research and Development Laboratory (USAMBRDL) is responsible for recommending ambient water quality criteria for munition production and handling facilities. To make such recommendations, USAMBRDL must know the environmental impact of pollutants generated at these facilities and the potential hazards associated with their discharge.

Hazard assessment for a chemical requires specific information about its concentration in the environment and its toxicity, as well as about the population likely to be exposed. The environmental fate of a chemical can be predicted as a function of time and location by use of a series of kinetic and equilibrium equations that describe the rates of dominant loss processes (photolysis, hydrolysis, etc.) under specific environmental conditions. These equations help to identify the major compartments in which a chemical is distributed and when coupled with the environmental conditions that represent the point of discharge, the persistence of a chemical can be assessed.

SRI International has developed a methodology and a computer model* to predict the environmental fate of pollutants in various aquatic systems based on laboratory measurements of specific environmental processes. This model integrates kinetic and equilibrium data for microbiological and chemical transformations with physical transport pathways in a multicompartment aquatic model to predict the concentration and the dominant processes that transform and transport organics in aquatic systems. The model can predict steady-state or time-dependent concentrations of discharged pollutants so that, together with toxicity and exposure information, a hazard evaluation can be made.

* A modified version of this model (EXAMS) is now available from EPA (Athens) and will be used for fate assessment.

Phase I of this study was to perform a literature review on 11 munition wastewater constituents to identify possible environmental fate processes and to obtain kinetic and equilibrium data for these processes that might be used to estimate persistence according to the SRI model. From this review, any gaps in the knowledge would be revealed, defining those areas where further work is needed.

USAMBRDL grouped the munition wastewater constituents into three categories by priority. The chemicals in Category I are 2,4,6-trinitrotoluene (2,4,6-TNT), RDX (1,3,5-trinitrohexahydro-1,3,5-triazine), 2,4-dinitrotoluene (2,4-DNT), and trinitroglycerine (TNG). Category II chemicals are 1,3-dinitrobenzene (1,3-DNB), 2,6-dinitrotoluene (2,6-DNT), 1,3,5-trinitrobenzene (1,3,5-TNB), and 2,3,6-trinitrotoluene (2,3,6-TNT). Category III comprises 2-amino-4,6-dinitrotoluene (2-A-4,6-DNT), 5-amino-2,4-dinitrotoluene (5-A-2,4-DNT), and 3,4-dinitrotoluene (3,4-DNT). These chemicals emanate primarily from the TNT manufacturing industry and from load, assemble, and pack facilities as well as from RDX and TNG production facilities. This review, and the subsequent studies proposed, are designed to aid the Army in defining water quality criteria at munition facilities and in guiding its pollution abatement programs.

LITERATURE REVIEW METHODOLOGY

The published literature was surveyed using both computer and manual search methods. The computer searches included such data bases as Chemical Abstracts (1972-1979), TOXLINE, NTIS Reports (1964-1978), Biological Abstracts (1969-present), POLLUTION, ENVIROLINE, ENVIROBIB, and AGRICOLA. The chemical name was used as the key word to obtain article titles and abstracts. The indices to chemical abstracts from 1906 to 1978 were scanned manually under each chemical's heading for key words related to transport and transformation processes. Relevant articles were obtained from those abstracts that appeared promising.

Also reviewed in this survey were monthly and final reports on past and current contracts supported by the USAMBRDL on transport and transformation processes of the subject chemicals.

The objective of the literature review was to obtain specific data on the physical properties and rate processes of the 11 compounds relevant to environmental transformation processes at Army discharge sites. These data are the necessary components of environmental fate modeling. The specific physical properties and rate constants investigated, along with their relevance to the determination of environmental fate, were:

- Solubility in water--Necessary for the determination of meaningful rate constants and sorption partition coefficients and for estimation of the Henry's law constant.
- Vapor pressure--Necessary for estimation of the Henry's law constant, which in turn can be used to estimate the volatilization rate of a chemical from water.
- Sorption and biouptake partition coefficients--Indicate how strongly the chemical will partition to soils, sediments, and biomass.

- Volatilization rate constant from water--Used to estimate how rapidly a chemical will volatilize under conditions representative of different freshwater aquatic systems.
- Absorption spectrum at wavelengths greater than 290 nm--Necessary for determination of the potential for direct photochemical transformation in the environment.
- Quantum yield--Measures the efficiency of a photochemical process; necessary for the calculation of the photochemical rate constant.
- Photochemical rate constant--Kinetic rate constant derived from the quantum yield, absorption spectrum, and light intensity; gives the rate of photolysis of a chemical in sunlight.
- Hydrolysis rate constant--Kinetic rate constant from which the rate of loss of a chemical due to hydrolysis can be determined under relevant environmental conditions (pH, temperature, etc.).
- Oxidation or reduction rate constant--Kinetic rate constants from which the rate of loss of a chemical due to oxidation or reduction processes can be determined under environmental conditions.
- Biodegradation rate constant--Kinetic rate constant from which the rate of loss of a chemical due to biotransformation can be determined.

RESULTS

SUMMARY

Although the literature on the chemistry of the majority of the compounds is abundant, little of it relates directly to the data necessary to determine environmental fate. Most of the data concern physical transport processes as summarized in Table 1. Some of these data are insufficient for the proposed assessment, so laboratory studies are necessary to measure the property or constant. Detailed evaluations and citations to the literature on nitro compounds are presented in the sections on each chemical.

Table 2 summarizes the kinetic data for hydrolysis and photolysis transformation processes including equilibrium constants for the addition of hydroxide ion. Table 3 is a summary of biotransformation processes. These transformation processes are detailed for each chemical in the subsequent sections.

CATEGORY I CHEMICALS

2,4,6-Trinitrotoluene (2,4,6-TNT)

Summary and Recommendations

A volatilization rate constant for 2,4,6-TNT can be estimated from extrapolated values of vapor pressure to calculate Henry's law constant. This estimate should be verified by laboratory studies.

Data from the literature suggest that sediment adsorption should not be significant. However, experiments were not performed under total equilibrium conditions, and a trend toward irreversible adsorption was noted. Further studies are needed to define the partitioning processes for 2,4,6-TNT.

Photolysis is projected to be a significant fate process. 2,4,6-TNT has uv absorption above 290 nm, and molar absorptivity needs to be

Table 1

SUMMARY OF PHYSICAL PROPERTIES, SORPTION PARTITION COEFFICIENTS, AND VOLATILIZATION
RATE CONSTANT RATIOS AT 20° C FOR THE ELEVEN MUNITION WASTEWATER CONSTITUENTS

Compound	Solubility (moles/liter)	Vapor pressure (torr)	Henry's law constant, H_c (torr M^{-1})*	Volatilization Half-life (days)	Sorption partition coefficient K_{oc}
2,4,6-TNT	5.4×10^{-4}	1.0×10^{-4} [†]	0.18 [†]	990	190 [†]
RDX	2.0×10^{-4}	4.1×10^{-9} ^{**}	2.0×10^{-5} ^{**}	9×10^6	420 [†]
TNG	5.3×10^{-3}	10^{-2} - 10^{-4}	>0.06	~ 3000	32*
2,4-DNT	1.5×10^{-3}	5.1×10^{-3}	3.4	47 (410) ^{††}	87*
1,3-DNB	2.2×10^{-3}	3.9×10^{-3}	1.8	73 (550) ^{††}	64*
1,3,5-TNB	1.5×10^{-4}	2.2×10^{-4}	1.5	130	520*
2,6-DNT	no data (1×10^{-3})*	0.018	18	9* (140) ^{††}	100*
2,3,6-TNT	No data	No data	No data	< 1500*	No data
2-A-4,6-DNT	No data	No data	No data	No data	No data
3,4-DNT	No data	No data	No data	No data (500) ^{††}	
5-A-2,4-DNT	No data	No data	No data	No data (2800) ^{††}	No data

* Estimated values.

† Extrapolated value for supercooled liquid.

‡ Measured value for K_p , but organic content of sediment is not known.

** Extrapolated value for solid.

†† Estimated from Spanggard's data (1978), assuming the relative humidity was 75%.

Table 2

SUMMARY OF TRANSFORMATION PROCESSES FOR NITRO COMPOUNDS AT 20 TO 25° C

Compound	Hydrolysis* (k_h in $M^{-1}s^{-1}$ or s^{-1})	Photolysis† (k_p in s^{-1})	K_{OH} Equilibrium Constant† (in M^{-1})
2,4,6-TNT	—	—	—
	$k_A [H^+] < 4.7 \times 10^{-9}$ (30°)	Prod. (SL, AL)**	0.4-3.7
RDX	$k_N < 4.7 \times 10^{-9}$ (30°)	—	—
	$k_B = (3.9 \pm 0.2) \times 10^{-3}$	$k_p = (1.7-2.8) \times 10^{-3}$	—
TNG	$k_A = 1.6 \times 10^{-6}$ (37°)	Prod. (AL)	—
	$k_N = 6 \times 10^{-6}$ (80°)	—	—
	$k_B = 2.1 \times 10^{-2}$	—	—
2,4-DNT	—	Prod.; $k_p = 2.8 \times 10^{-5}$ (pH 3), 1.4×10^{-4} (pH 10)	7.9×10^{-4}
1,3-DNB	—	$k_p < 10^{-7}$; k_p (rel)†† < 0.01	1.6×10^{-3}
2,6-DNT	—	$k_p = 2.0 \times 10^{-5}$; k_p (rel) ~ 3.6	$< 1 \times 10^{-7}$
2,3,6-TNT	—	—	—
3,4-DNT	—	k_p (rel) < 0.01	—
1,3,5-TNB	—	k_p (AL) < 8×10^{-3}	0.4 $K_{SO_3} = 3.7 \pm 0.4$
5-A-2,4-DNT	—	k_p (rel) ≈ 1.0	—
2-A-4,6-DNT	—	k_p (AL) = 1.7×10^{-1}	—

* Hydrolysis applicable only to RDX and TNG.

† All nitro compounds listed exhibit some tailing in uv spectrum above 290 nm. Rate constant k_p is calculated from $k_p = \ln(C_0/C)/t$ and is averaged over 24-hr day. All rate measurements are in sunlight, unless otherwise indicated by AL (artificial light).‡ Equilibrium constant for the process $AR(NO_2)_x + B \rightleftharpoons AR(NO_2)_x$. Prod. - product analysis reported.

** SL, sunlight; AL, artificial light.

†† k_p (rel) is rate constant for photolysis in sunlight relative to rate constant for 5-A-2,4-DNT.

Table 3
SUMMARY OF DATA FOR BIOTRANSFORMATION OF NITRO COMPOUNDS

Compound	Type of Test	Inoculum	Media	Initial Concentration mg l ⁻¹	Disappearance Rate or Percentage of Decrease
2,4,6-TNT	Shaker flask	Acclimated culture or waters and soil	Trypticase soy broth or basal salts and glucose or yeast extract	10 or 100	> 99% in 5-6 days
	Shaker flask	Sediment	Basal salts	10	6.7-9.4 mg l ⁻¹ in 5 days
	High cell concentration	Isolat	Basal salts	100	94 mg l ⁻¹ in 18 hr
	Static crock	River water	River water	20	18 mg l ⁻¹ in 30 days*
	Oxidation ditch	Activated sludge	Corn steep nutrient	10-50	97 ± 2%†
RDX	Photosynthetic bottle	Photosynthetic bacteria	Basal salts + acetate	20	19 mg l ⁻¹ in 5 days
	Flask	Water + sediments	Water + sediments	11	8 mg l ⁻¹ in 27-33 days
TNG	Shaker flask	Activated sludge	Basal salts + glucose	67	54% in 5 days
	Chemostat	Activated sludge	Basal salts + ethanol + ether	30	100%‡
2,4-DNT	Shaker flask	Fungi	Basal salts + glucose	100	---
1,3-DNB	Two-stage, continuous	Azotobacter and sludge	Basal salts + glucose	136	98%
2,6-DNT	No data				
2,3,6-TNT	No data				
3,4-DNT	No data				
1,3,5-TNG	Two-stage, continuous	Azobacter and sludge	Basal salts + glucose	136	100%
5-A-2,4-DNT	No data				
2-B-4,6-DNT	Shaker flask	Activated sludge	Corn steep nutrient	13	13 mg l ⁻¹ in 3 days

* Pseudo first-order rate constant, 0.087 day⁻¹.

† Feed rate of 0.25 - 8 liter/min.

‡ Residence time of 8-15 hr.

measured in the solar region. Detailed rate studies are necessary, as are studies on the effect of pH on the photolysis rate.

Biotransformation may also be a significant fate process for 2,4,6-TNT. Both degradation rate studies with enrichment cultures obtained from natural waters and studies in the presence of sediments are necessary. Reduction of the nitro group appears to be the primary step in the transformation of 2,4,6-TNT, so both aerobic and anaerobic transformation studies may be important. Studying biotransformation in the presence of light may also elucidate the ultimate fate of 2,4,6-TNT.

Physical Properties

Solubility in Water

The solubility of 2,4,6-TNT in water at 20° C reported by Urbanski (1964), 0.0130 g/100 g of water (5.7×10^{-4} M, 130 ppm), agrees well with the value of 117 ppm (5.2×10^{-4} M), which was recently measured by Spanggord (1977). The average of these values is 124 ppm (5.4×10^{-4} M). The values of 86 and 83 ppm at 21° C, reported by Battelle (1978), are probably erroneous because the saturated solutions were filtered before analysis; the filter may have adsorbed some of the dissolved TNT.

Vapor Pressure

The vapor pressure of solid 2,4,6-TNT was measured by Pella (1977), who used a gas saturation technique. His data fit the equation

$$\log_{10} P(\text{torr}) = (12.31 \pm 0.34) - (5175 \pm 105)/T$$

At 25°, the vapor pressure of solid TNT measured by Pella was

$$8.02 \times 10^{-6} \pm 0.16 \times 10^{-6} \text{ torr.}$$

Maksimov (1968) obtained data using 2,4,6-TNT when it was near its boiling point. Reasonable estimates for the extrapolated vapor pressure of the supercooled liquid are 1.7×10^{-4} torr at 25° C and 1.0×10^{-4} torr at 20° C.

Nitta et al. (1950) measured the vapor pressure of TNT over a temperature range of 68 to 88° C using a modified Knudsen technique. Those data can be extrapolated to 20° C, giving values of 4.5×10^{-3} torr (solid) and 2.8×10^{-4} torr (liquid).

Physical Transport

Volatilization Rate from Water

A value of the Henry's law constant, H_c , for a chemical can be calculated using the equation

$$H_c = P_{sl}/C_{sat} \quad (1)$$

where P_{sl} is the vapor pressure of the supercooled liquid and C_{sat} is the solubility of the chemical in water. For 2,4,6-TNT,

$$H_c = 1.0 \times 10^{-4} / 5.2 \times 10^{-4} = 0.18 \text{ torr } M^{-1}$$

Because the value of H_c is much less than $10 \text{ torr } M^{-1}$, we predict that the volatilization rate of 2,4,6-TNT will be limited by mass transport resistance in the gas phase.

The literature search revealed no measurements of the volatilization rate of TNT. The estimated value of the volatilization rate constant in the environment, $(k_v^C)_{env}$, is estimated from equation (2)*

$$(k_v^C)_{env} = \left(\frac{M^W}{M^C} \right)^{1/2} \frac{H_c}{L_{env}} \frac{(k_g^W)_{env}}{RT_{env}} \quad (2)$$

where

M^W = molecular weight of water

M^C = molecular weight of the chemical

$(k_g^W)_{env}$ = mass transport coefficient of water in the environment

L_{env} = depth of the water body

* See Appendix A for the development of volatilization rate equations.

Using values of $(k_g^W)_{env} = 2100 \text{ cm hr}^{-1}$, and $L_{env} = 200 \text{ cm}$,
 $(k_v^C)_{env}$ is

$$(k_v^C)_{env} = \left(\frac{18}{M^C} \right)^{1/2} \frac{H_c (2100)}{(200) (62.4) (293)}$$

$$= 2.44 \times 10^{-3} H_c (M^C)^{-1/2} (\text{hr}^{-1})$$

$$= 2.44 \times 10^{-3} (0.18) (227)^{-1/2}$$

$$= 2.9 \times 10^{-3} \text{ hr}^{-1}$$

$$t_{1/2} = \ln 2 / k_v^C$$

$$= 990 \text{ days}$$

This is an approximate estimate, and, because of the assumptions required to make the estimate, it could be in error by an order of magnitude or more. Screening studies of the volatilization of 2,4,6-TNT are recommended.

Sorption on Soils and Sediments

Syracuse Research Corporation (1978a,b,c) measured TNT sorption on four sediments and obtained K_p values of 5.5 to 19.3 after 24-hour equilibration times. These partition coefficients indicate that sorption is not a significant fate for TNT, because strongly adsorbed materials have partition coefficients greater than 100. The adsorption experiments indicated that adsorption equilibrium was not fully obtained in 24 hours, but they did not elucidate the mechanism or estimate the extent of the continued adsorption. The sediments used were not characterized, so we cannot predict sorption partition coefficients for other sediments.

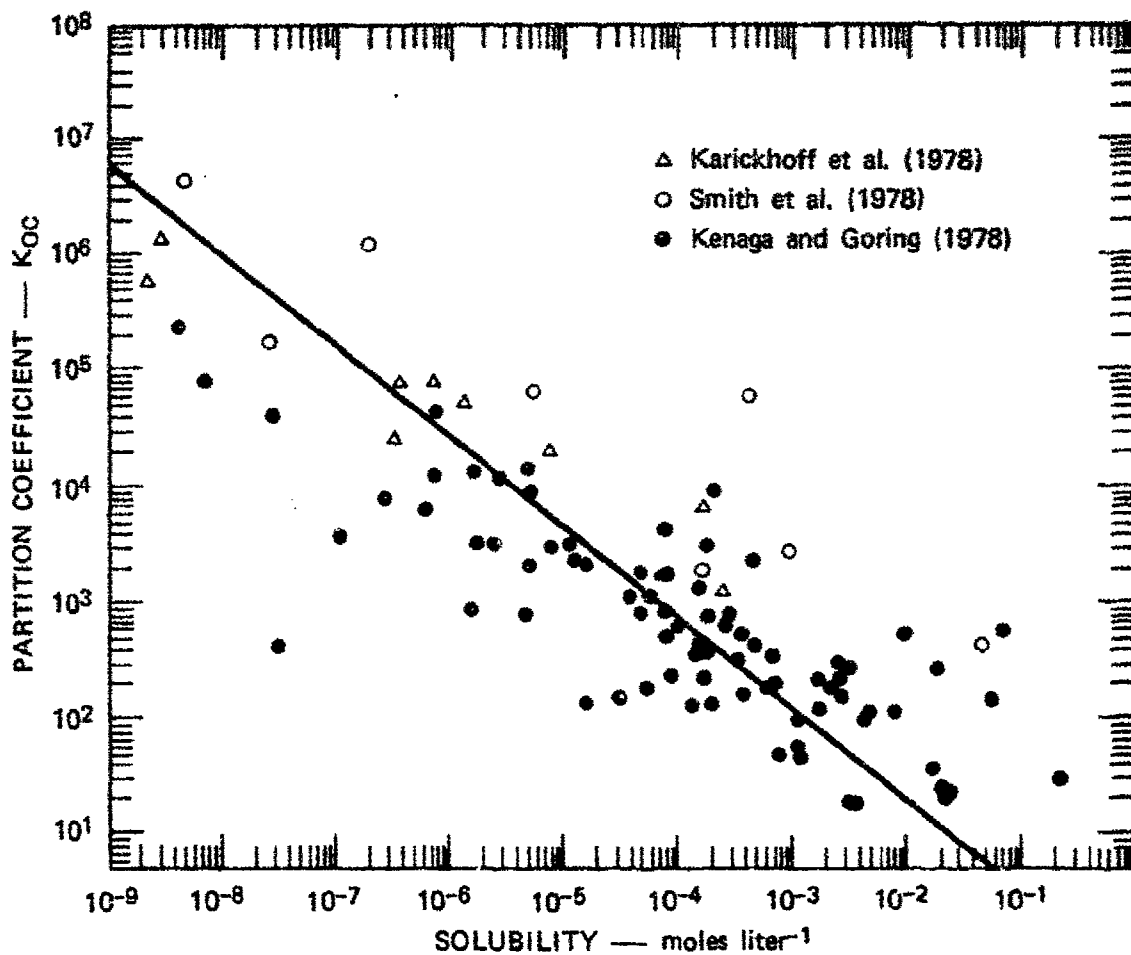
Battelle (1978) conducted soil column tests to determine whether TNT migrates into groundwater. However, the experiments were terminated before enough data were collected to determine migration rates. The experiments cannot be used to determine partition coefficients.

Karickhoff et al. (1978) and Kanaga and Goring (1978) have shown that sediment and soil partition coefficients are strongly correlated with the organic carbon contents of the soil and with the solubility of the chemical in water. Figure 1 summarizes their data, as well as data obtained by Smith et al. (1978). These results suggest that the value of $K_{oc} = K_p / F_{oc}$ can be estimated from Figure 1 within about an order of magnitude. The equation for the line representing the linear least-squares fit to the data is

$$\log K_{oc} = -0.27 - 0.782 \times \log(\text{solubility, M}). \quad (3)$$

Using the average solubility of 5.4×10^{-4} M, the predicted value of K_{oc} is 190. Using a value $F_{oc} = 0.07$, which is "typical," the predicted value of $K_p = K_{oc} F_{oc} = (190)(0.07) = 13.3$.

Additional sorption experiments are recommended to determine how the partition coefficient is related to sediment and soil properties and how extended contact times affect the partition coefficient.



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FIGURE 1 SOIL OR SEDIMENT PARTITION COEFFICIENT OF CHEMICALS VERSUS SOLUBILITY IN WATER

UV Absorption Spectrum > 290 nm

Schroeder et al. (1951) reported that in ethanol solvent, 2,4,6-TNT has an absorption coefficient of $\sim 10^3$ at 310 nm; the data do not extend beyond 320 nm. Abe (1959) measured the UV spectra of 2,4,6-TNT in several solvents in the range of 300 to 400 nm. In water, absorption coefficients were approximately 650, 250, and 30 $M^{-1} \text{ cm}^{-1}$ at 300, 350, and 400 nm, respectively.

Photolysis

Burlinson (1978) has studied the photolysis of TNT in a natural river water and in distilled water. He found that in the sunlit natural water (pH 8.2; TOC, 4.48 mg/liter), the TNT concentrations neared zero after 6 to 8 days; in the dark, the same solution required 30 days for 90% loss of TNT. The products identified from the natural water reaction were 1,3,5-TNB, 2,4,6-trinitrobenzaldehyde (TNBAL), and three biotransformation products (amino nitro compounds). 1,3,5-TNB was the major product formed, with a 10% yield obtained after 8 days; yields of 1,3,5-TNB were subsequently reduced by biotransformation. Burlinson also reported that TNBAL in the river water was 85% converted to 1,3,5-TNB in 30 minutes, but the reason for this rapid conversion of TNBAL to 1,3,5-TNB is not known. In distilled water, photolysis of TNT produced only TNBAL.

Burlinson and Glover (1976) reported earlier that photolysis of 141 ppm TNT at > 290 nm was more rapid in Mississippi River water than in distilled water; they attributed the rate difference to the higher pH of the river water, which changed from pH 7.1 to 6.8 during the photolysis. This was similar to the observation of Burlinson et al. (1973) that 60 minutes of photolysis of TNT at > 290 nm in D_2O gave 3, 48, and 70% losses of TNT at pH 1.1, 3.0, and 6.0, respectively. In the TNT recovered from the pH 1.1 and 6.0 solutions after the photolysis, deuterium incorporations were 75 and 50%, respectively.

In that 1973 study, Burlinson et al. also examined "pink water," which was prepared by exposing saturated 120- to 130-ppm solutions of

TNT to a Hg lamp source filtered by borosilicate glass. The pink water contained as products TNBAL, 1,3,5-TNB, 2,4,6-trinitrobenzonitrile, and 4,6-dinitroanthranil. Burlinson et al. also found that when TNT in an aqueous solution was exposed to sunlight for 4 days (30 hours of sunlight), about 75% loss of starting material occurred and an additional four substituted azoxybenzene compounds were produced. Only 20% of the products were obtained in the benzene extract of this pink water solution. When the TNT photolysis was performed in tetrahydrofuran solvent, a 47% yield of azoxy compounds was obtained, and the authors reasoned that the formation of azoxybenzene compounds in pink water must also require a hydrogen atom donor.

Burlinson and Glover (1977a) have also reported that TNT photoproducts in photolyses at > 290 nm were not significantly different when the initial concentrations were 113 and 4.5 ppm. In a subsequent report (1977b), they did find that photoproducts were different depending on whether the Hg lamp source had the borosilicate filter. In contrast, Spanggard et al. (1978) found no significant difference in photoproducts from TNT photolyses performed using sunlight or a borosilicate-filtered Hg source.

Suryanarayanan and Capellos (1972, 1974) investigated the photolysis of TNT using flash photolysis techniques. They found that the formation or decay rates of the aci-quinoid intermediates were unaffected by the presence of molecular oxygen. In nonpolar solvents (benzene or cyclohexane), the absorption maximum was at 460 nm, with a decay rate constant of $1.04 \times 10^3 \text{ sec}^{-1}$. In polar solvents (methanol or acetonitrile), λ_{max} were found at 500, 540, and 630 nm. Decay rate constants of the transient were measured as 1.74 sec^{-1} in methanol and 0.44 sec^{-1} in acetonitrile solvents. In the 1972 report, the authors also wrote that the aci-quinoid TNT isomer has a pK_a of -0.93 .

Sandus and Slagg (1972) have reported a disappearance quantum yield of 1×10^{-3} for the photolysis of 2,4,6-TNT in heptane solution at 254 nm, with the quantum yield independent of oxygen. The authors

also measured a mean lifetime of 1.5 ± 0.3 msec for the TNT intermediate formed in a flash photolysis experiment; the maximum absorption for the intermediate was about 470 nm.

Hydrolysis

No hydrolysis of 2,4,6-TNT is expected under environmental conditions.

Biodegradation

The microbial degradation of 2,4,6-TNT has been a subject of interest since the 1940s. Rogovskaya (1951) observed biological decomposition of TNT at the 5-mg/liter level. He reported that TNT concentrations of 0.5 to 1.0 mg/liter have negligible effects of stream self-purification, but increasing concentrations inhibit it.

Using phenol-adapted mixed bacteria from soil, compost, or mud, Chambers et al. (1963) evaluated the biodegradation of many aromatic compounds by respiratory techniques. They observed a slow but significantly higher oxygen uptake rate with 2,4,6-TNT at 100 mg/liter than endogenous respiration, indicating TNT is oxidized.

Enzinger (1970) adapted organisms from sewage treatment plant samples to 2,4,6-TNT. When 100 ppm TNT was incubated with those organisms in trypticase soy broth, the concentration decreased to 1.25 ppm in 5 days. The cells had only trace amounts of 2,4,6-TNT, so the decrease was not due to adsorption.

Bringmann and Kuehn (1971) used a two-stage model wastewater purifier; the first stage was an aerator with Azotobacter agilis, and the second was an overflow basin with activated sludge. They reported that 128 mg/liter 2,4,6-TNT was 99.6% transformed after the second stage.

Osmon and Klausmeier (1972) reported that TNT was degraded in agar plates or flasks when other organic nutrients were added to the media. Flasks containing 100 ppm TNT, mineral salts, and yeast extract inoculated with sewage effluents, soil, or pond water gave

> 99% loss of TNT after 6 days. No TNT disappearance was observed in inoculated flasks containing only mineral salts and 2,4,6-TNT. Klausmeier et al. (1973) then tested gram-negative bacteria, actinomycetes, yeasts, and fungi. They found that TNT at 50 mg/liter severely inhibited the growth of these organisms in most cases. However, many of the cultures did grow well and degraded TNT at lower concentrations with other organic nutrients. In studying treatments of TNT wastewater, Nay et al. (1974) found that TNT waste can be biologically treated when combined with domestic waste. TNT was removed by biodegradation and biosorption.

Evidence of organisms using TNT as a sole carbon source was first reported by Won et al. (1974). TNT enrichment cultures from mud and water could grow in TNT and basal salts, and they degraded the TNT. For accelerated TNT degradation, the addition of glucose or yeast extract was essential. Complete dissimilation of 80 mg/liter TNT within 24 hours occurred in medium supplemented with 0.5% yeast extract. In the medium filtrate, TNT was metabolized to 2,2',6,6', tetranitro-4-azoxytoluene (4-Az), 2,2',4,4'-tetranitro-6-azoxytoluene (6-AZ), 2-amino-4,6-dinitrotoluene (2-A-4,5-DNT), 4-hydroxylamino-2,6-dinitrotoluene (4-OHA-2,6-DNT) and nitrodiaminotoluene. Azoxy compounds disappeared at later stage of incubation. 4-Amino-2,6-dinitrotoluene (4-A-2,6-DNT) was not found. According to Channon et al. (1944), the azoxy compounds may be formed by a coupling reaction of the corresponding hydroxylamines and are not the direct metabolic products of TNT.

Traxler et al. (1974) also reported that gram-negative bacteria isolated from various sources can use TNT as the sole source of nitrogen and carbon. They also reported that addition of yeast extract at 100 µg/ml stimulated microbial growth on TNT. With an isolate mutant, 62% of the TNT was removed from a medium containing yeast extract and 100 µg/ml TNT in 20 hours. The presence of nitrite in the medium indicated removal of the nitro group from the ring. Using ring-labeled ¹⁴C-TNT, Traxler and his co-workers demonstrated the incorporation of TNT into the cellular material by two isolates. Release of ¹⁴CO₂ was observed, and they concluded that cleavage of

the benzene ring occurred. However, the $^{14}\text{CO}_2$ activities were very low (0.3 to 1.2% of added ^{14}C -TNT). To explain this phenomenon, Traxler et al. conducted heterotrophic CO_2 fixation experiments with $\text{NaH}^{14}\text{CO}_3$ and found that CO_2 was taken up by the cells when the organisms were growing on unlabeled TNT. On a molar basis, CO_2 fixation accounted for at least 41% of the TNT consumed.

In addition, Traxler (1975) demonstrated that ^{14}C activity from metabolized ring ^{14}C -TNT was in ninhydrin-positive materials obtained from the hydrolysis of cellular protein. He used washed cells at high concentrations and found that they effectively removed TNT from the media with or without yeast extract, or other organic nutrients; 94% TNT was removed from 100 $\mu\text{g/ml}$ in 18 hours with 14 mg/ml cells. At low cell concentrations, the removal was poor.

In a shaker flask with TNT-enriched medium Weitzel et al. (1975) reported that sediment bacteria transformed TNT without additional organic materials. TNT was reduced 6.7 to 9.4 mg/liter from 10 mg/liter in 5 days. The addition of glucose and peptone and fatty acids increased the formation of transformation products. Disappearance of TNT was 9.9 mg/liter from 10 mg/liter in 5 days. The metabolites found were similar to the products reported by Won et al. (1974).

Using an enzyme preparation from Veillonella alcalescens, McCormick et al. (1976) tested a variety of nitroaromatic compounds, including 2,4,6-TNT, for their reduction by hydrogen to form corresponding arylamines. The relative rate of reduction to other nitroaromatics was measured. McCormick et al. showed that TNT can be degraded by anaerobic microorganisms as well as aerobic organisms. Jerger and Chynoweth (1966) reported the anaerobic microbial degradation of TNT. In benchtop anaerobic digesters, they observed partial disappearance of TNT and the appearance of transformed products, one of which was identified as 4-OHA-2,6-DNT. Parrish (1977) tested 190 pure cultures of fungi and reported that 183 strains were able to transform 2,4,6-TNT in a medium containing 100 mg/liter TNT, glucose, and basal salts. Enzyme activities were in mycelia and not in

culture filtrates. The transformation products were 4-A-2,6-DNT, 4-OHA-2,6-DNT, and 4,4'-azoxynitrotoluene. Studies with ring-labeled ^{14}C -TNT gave no evidence for cleavage of the carbon skeleton.

Carpenter et al. (1978) used an activated sludge system to investigate the fate of ^{14}C -labeled 2,4,6-TNT. ^{14}C -TNT was not detected in the aerated reactor and no significant $^{14}\text{CO}_2$ was formed; the radioactivity was found in both the floc and supernatant. However, the ^{14}C in microflora was not the characteristic constituent of lipid and protein material (fatty acids and amino acids), but it was bound to these compounds as polyamide macromolecules. No evidence indicated that the nucleus was cleaved. In a 3-year study of a 3000-gallon pilot-scale treatment facility, Hoffsommer et al. (1978) used a variety of conditions to degrade TNT and obtained the best results with activated sludge microorganisms and supplemental nutrients. With TNT at 10 to 50 ppm, 97% of the TNT was removed at a feeding rate of 8 to 0.25 liters/minute. Using labeled TNT, Carpenter et al. (1978) obtained similar results. The metabolites found were 4-A-2,6-DNT, 2-A-4,6-DNT, 2,4-diamino-6-nitrotoluene, and 2,6-diamino-4-nitrotoluene.

Burlinson (1978) conducted river die-away degradations of TNT with river water. The experiments were conducted in the dark and in sunlight under aerobic conditions. Under darkness, 90% of the TNT (initially 20 ppm) disappeared in 30 days. The data indicated that the transformations were first order relative to TNT concentration ($.087 \text{ day}^{-1}$) (without lag periods). Although microbiological plate counts were made, the fraction of the microbial population responsible for TNT transformation was not known. ATP analysis of the waters was conducted, but the concentration found did not correspond to the biomass. In sunlight, TNT transformed much faster, suggesting that photodegradation occurs at a faster rate than biotransformation.

1,3,5-TNB was found in the photolysis with river water; photolysis of TNT in distilled water produced TNBAL. Under both darkness and light conditions, the biotransformation products 2-A-4,6-DNT and

4-A-2,6-DNT were found, but the concentrations were higher in the experiments conducted in the dark. 3,5-Dinitroaniline (3,5-DNA) was found in the sunlight conditions and appeared to be the biotransformation product of TNB.

In summary, 2,4,6-TNT is biotransformable by microorganisms including bacteria, yeast, and fungi, although TNT inhibits their growth at high concentrations. For many of the organisms tested, additional organic nutrients are essential. For others, added nutrients are helpful in the transformation of TNT when it is used as the sole carbon and nitrogen source. Burlinson's data (1978) show that biodegradation is a first-order loss of TNT in river die-away tests, but no rate study was conducted with an enriched culture. Reduction of the nitro group to the amino group seems to be the first step in biotransformation. Both the ultimate degradation of TNT to CO₂ and evidence for ring cleavage were reported by Traxler and his co-workers (1974), but no evidence for either reaction was found by Carpenter et al. (1978) or Hoffsommer et al. (1978).

1,3,5-Trinitrohexahydro-1,3,5-Triazine (RDX)

Summary and Recommendations

The volatilization rate of RDX, estimated from the available literature data, suggests that volatilization should not be a significant environmental fate. A screening study should be performed to validate the predictive method, however.

Sediment adsorption is not expected to be a significant fate process for RDX because of low partition coefficients determined for various sediments.

Photolysis appears to be a rapid process, and detailed rate studies in natural waters are needed. A reaction quantum yield for RDX at a wavelength above 290 nm as well as its uv absorption spectrum above 290 nm should also be measured for use in calculation of rate constants for direct photolysis in aquatic systems.

Hydrolysis of RDX at environmentally relevant pH values is slow. Detailed hydrolysis studies are not recommended unless the screening studies from other fate processes show a half-life for RDX of greater than 170 days.

Biotransformation studies of RDX need to be performed. They should include the development of enrichment cultures, the function of sediment in biotransformation, the use of RDX as a sole carbon source, and the identification of metabolic products.

Physical Properties

Solubility in Water

Spanggord (1977) determined that the solubility of RDX in water at 18° C was 44.7 ppm (2.0×10^{-4} M). Syracuse Research Corporation (1978) reported a solubility of 42 ppm (1.9×10^{-4} M) at 20° C-- in excellent agreement with Spanggord's result. The values reported by Battelle Columbus Laboratories (1978), 24 and 18 ppm at 21° C, are probably erroneous because the saturated solutions were filtered before analysis. The filter probably adsorbed some of the dissolved RDX.

Vapor Pressure

Using a Langmuir method, Rosen and Dickinson (1969) determined the vapor pressure of solid RDX over the temperature range of 56 to 98° C; the extrapolated vapor pressure at 20° C was 4.1×10^{-9} torr. Edwards (1953) used a Knudsen method, and the extrapolated vapor pressure was 8.2×10^{-9} torr at 20° C. This value is probably less valid than that of Rosen and Dickinson because Edwards used a narrower temperature range (110 to 138° C).

Physical Transport

Volatilization Rate from Water

An estimate of the Henry's law constant for RDX using the data of Rosen and Dickinson and of Spanggord is 2.0×10^{-3} torr M^{-1} .

That constant is very low, and the correct value of H_c may be an order of magnitude higher. The calculated value of $(k_v^C)_{env}$ is $3 \times 10^{-5} \text{ hr}^{-1}$ and the estimated half-life for volatilization is 9×10^6 days. Volatilization should not be a significant environmental fate for RDX and volatilization studies are not recommended.

Sorption on Soils and Sediments

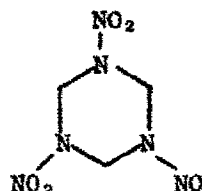
RDX sorption was measured on three sediments (Syracuse Research Corporation, 1977a,b; 1978a). The measured partition coefficients varied from 4.2 for a highly organic sediment to 0.8 for a sandy loam. These values indicate that RDX is only weakly adsorbed to sediments, and the experiments did not show increases in adsorption with extended contact times.

Battelle Columbus Laboratories (1978) conducted soil column tests to determine whether RDX migrates into groundwater. Unfortunately, the experiments were terminated before enough data were collected to determine migration rates and the experiments cannot be used to determine adsorption partition coefficients. Nevertheless, RDX sorption apparently does not change with increased contact time, so additional experiments to study the nature of the interaction of RDX and soil or sediment are not required.

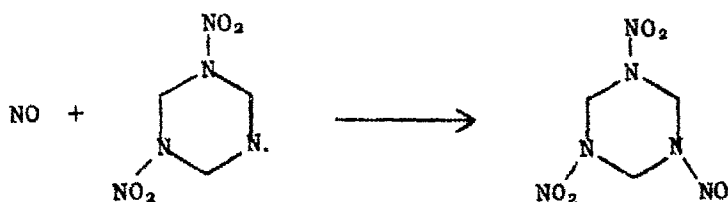
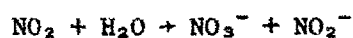
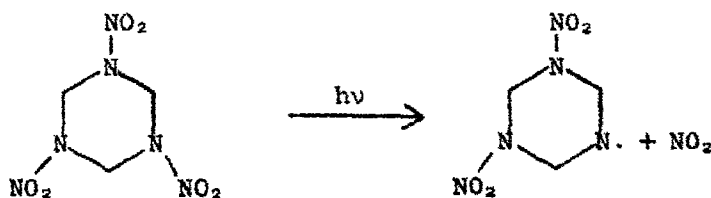
Photolysis

Spanggord et al. (1978) reported that of 44 ppm RDX in aqueous solution, about 50% lost after exposure to sunlight for 7 days. Syracuse Research Corporation (1978c) reported that 12 ppm RDX in aqueous solution had a half-life of 10.7 hours; they noted that this half-life compared favorably with half-lives of 9 to 13 hours that were previously determined.

Kubose and Hoffsommer (1977) found that the major product from photolysis of RDX at $> 280 \text{ nm}$ in acidic aqueous solution was the mononitroso analog of RDX.



The product formation was independent of the oxygen concentration in solution, and this product was not found in neutral or basic media. The authors suggested the initial step was photolysis of RDX to NO_2 and the azayl radical followed by the sequence of reactions shown below.



Kubose and Hoffsommer also reported that nitroso products were formed directly from photolyses of RDX at > 220 nm through cleavage of the N-O bond; the formation of nitroso product(s) under these conditions was independent of the pH of the solution. Syracuse Research Corporation (1978c) reported a quantum yield of 0.67 for photolysis of RDX at 254 nm in an aqueous solution, pH 8.1. The product formed was the

mononitroso analog of RDX, and the rate of photolysis was independent of oxygen. The work by Kubose and Hoffsommer (1977) suggests that N-N bond cleavage is the primary photochemical process at wavelengths greater than 280 whereas N-O cleavage occurs at shorter wavelengths. Hence, the quantum yield of 0.67, measured at 254 nm may not be relevant to photolysis of RDX in the environment.

Hydrolysis

Hoffsommer and Rosen (1973) have reported that RDX in seawater (pH ~ 8) at 25° C was 11.6% hydrolyzed in 108 days; this conversion rate is equivalent to a hydrolysis half-life of 1.7 years. A subsequent report by Hoffsommer et al. (1977) gives a second-order rate constant for alkaline (OH^-) hydrolysis of RDX at 25.0° C as $3.9 \pm 0.2 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$; using this rate constant, the calculated half-life for OH^- hydrolysis of RDX at pH 8.0 is 5.6 years. In the same report, Hoffsommer and his colleagues present data indicating that the hydrolysis half-life of RDX at pH 9 is 200 days. A Syracuse Research Corporation report (1978c) gives a rate constant of $1.6 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ for hydrolysis of RDX at pH 9.1 and 31° C. This information indicates that alkaline hydrolysis will not be an important process in aquatic environments compared with sunlight photolysis.

No reliable data on the neutral or acid hydrolyses of RDX are available. Information presented in a Syracuse Research Corporation report (1978a) indicates, however, that the half-life for RDX hydrolysis at 30° C will be greater than 170 days in the pH range of 2.1 to 7.1. Because the photochemical transformation of RDX in sunlight is rapid, neither neutral nor acid hydrolysis of RDX will be important processes in aquatic systems.

Biodegradation

Osmen and Klausmeier (1972) studied the biodegradation of TNT, RDX, and picrate. Some RDX disappearance was indicated during the soil enrichment studies, but proof of RDX degradation by microorganisms was not obtained.

Soli (1973) observed disappearance of RDX when it was incubated with purple photosynthetic bacteria. About 97% of RDX was transformed, from the initial concentration of 20 mg/liter, after 5 days of incubation. Soli hypothesized that rather than being metabolized, RDX is reduced by an electron "storm" during the photosynthetic process in the organisms.

In their pilot-plant study of TNT biodegradation, Hoffsommer et al. (1978) found no biodegradation of RDX either alone or in the presence of TNT. TNT bioconversion was not inhibited by the presence of RDX.

In an environmental fate study of RDX, Sikka et al. (1978) reported that 10 ppm RDX was decreased only when sediments were added to river waters in river die-away experiments, with about a 20-day lag period. During a 1-month period, no loss of RDX occurred in unsupplemented water samples or in samples that contained yeast extract. The evolution of $^{14}\text{CO}_2$ from ^{14}C -RDX was observed in water and water plus sediment after the lag phase. When ^{14}C was added to wastewater samples from HMX production lines with sediment, as high as 80% $^{14}\text{CO}_2$ was produced after 38 days of incubation, including 10 days of lag phase. Other river waters with sediments did not produce significant amounts of $^{14}\text{CO}_2$, despite their ability to transform RDX (nearly 80% loss from an initial level of 10 ppm). Whether the sediment in these experiments provides extra nutrients, essential nutrients, or cometabolic substrates or whether it provides more organisms needs to be studied further.

Trinitroglycerine (TNG)

Summary and Recommendation

A volatilization rate for TNG can be estimated from literature data and detailed studies are not recommended. Also, sediment adsorption is not believed to be a significant process based on estimates of the partition coefficient; however, screening studies are recommended. Photolysis studies should be performed to establish a limiting environmental photolysis rate for TNG. Hydrolysis of TNG under neutral and acidic conditions will be slow. A screening study is needed to determine a limiting rate constant at alkaline pH. Complete biotransformation rate studies are recommended to detail the importance of this fate process for TNG.

Physical Properties

Solubility in Water

The solubility of TNG in water is reported to be 1.0 g/800 ml of water (5.5×10^{-3} M, Merck Index) and 0.138 g/100 g of water (6.1×10^{-3} M) at 20° C (Ledbury and Frost, 1927).

Vapor Pressure

Kemp et al. (1957) reported that the vapor pressure of liquid TNG at 20° C is 2.0×10^{-2} torr. Yokogawa et al. (1966) measured a vapor pressure of 3.8×10^{-4} torr at 20° C. Vacek and Stanek (1959) report data from which the extrapolated vapor pressure of TNG at 20° C is 4.2×10^{-3} torr. Obviously, the agreement between these data is poor.

Physical Transport

Volatilization Rate from Water

Estimates of the Henry's law constant for TNG, using the various literature values are that H_c is between 3.3 and 0.06 torr M^{-1} . Using $H_c^C = 0.06$ torr M^{-1} , the estimated value of $(k_v^C)_{env}$ is about 10^{-3} hr $^{-1}$ and the half-life for volatilization is about 3000 days. Volatilization rate studies for TNG are not recommended.

Sorption on Soil and Sediments

No sediment or soil adsorption isotherm data for TNG were found during the literature search. Based on the solubility of TNG in water at 14% and the correlation of K_{oc} and water solubility shown in Figure 1, the estimated value of K_{oc} is 20. This value suggests that adsorption on sediments may not be a significant environmental fate. Nevertheless, screening experiments are recommended.

Photolysis

No data suitable for assessing the photolysis of TNG in aquatic systems are available. Urbanski (1947) found that TNG is decomposed to acidic products when irradiated in a quartz well/Hg lamp system.

Osada et al. (1965) reported that films of cellulose nitrate are decomposed by uv light and sunlight. By analogy to the sunlight photolysis of cellulose nitrate, TNG is also probably photolyzed in sunlight.

Hydrolysis

DiCarlo (1975) has reviewed the chemistry and biochemistry of TNG and notes that the mechanism of TNG hydrolysis is unknown. According to DiCarlo, kinetic and mechanism studies are difficult because of competitive side reactions that are hydrolytic, oxidative, and reductive in nature. Thus, the reaction of TNG in alkaline solution has been found to proceed by the following stoichiometry: $\text{TNG} + 5\text{KOH} \rightarrow \text{KNO}_3 + 2\text{KNO}_2 + \text{HCO}_2\text{K} + \text{CH}_3\text{CO}_2\text{K} + 3\text{H}_2\text{O}$. Glycerol was found as a hydrolysis product of TNG when the reaction was performed in the presence of a compound such as phenyl mercaptan, which is oxidized preferentially to glycerol.

Svetlov et al. (1976) have studied the kinetics of the neutral hydrolysis of several polynitrates of polyhydric alcohols, including TNG. The kinetic experiments were conducted with solutions of the nitrate esters in distilled water; nitric and nitrous acid were generated by the hydrolysis, so the kinetic data reported were based on the first 5% of the reaction. The rate constant measured for TNG hydrolysis at 80° C was $6 \times 10^{-8} \text{ sec}^{-1}$, which corresponds to a half-life of 134 days. Assuming that the rate of hydrolysis is halved for each 10° C decrease in temperature, the half-life for TNG hydrolysis at environmentally relevant temperatures will be on the order of years at neutral pH values (nominally pH 5 to 7).

Rosseel et al. (1974) measured the hydrolysis rate constants for TNG and its hydrolysis products at 37° C in 1 to 4 M HCl. In 1 M HCl, the respective hydrolysis rate constants for TNG, 1,3-dinitro-glycerine and 1-nitroglycerine were 1.6×10^{-6} , 3.7×10^{-7} , and $2.40 \times 10^{-7} \text{ sec}^{-1}$; the half-life for TNG under these conditions is 5.0 days. Assuming that the process studied was first order in both acid and

nitrate ester, the acid hydrolyses will be 10^4 slower at pH 3, with an acid hydrolysis half-life of over a century.

Capellos et al. (1978) thoroughly examined the alkaline hydrolysis of TNG and its derivative esters. The alkaline hydrolysis of TNG at 25° C was determined to have a second-order rate constant of $2.15 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ (average rate constant for two experiments). Using this rate constant, the half-life for alkaline hydrolysis of TNG at pH 9 is 37 days.

From these data, the hydrolysis half-life of TNG at 25° C is reliably predicted to be more than 1 year at pH 3 to 8; at pH values above 8, the hydrolysis half-life is less than 1 year; and the half-life at pH 9 is 37 days. Therefore, unless other transport or transformation processes are all unusually slow for TNG, hydrolysis of TNG will not be an environmentally significant fate process except possibly at high pH levels.

Biodegradation

Relatively little information has been published on the microbial degradation of TNG, although many papers reported the metabolism of this compound in mammalian systems (DiCarlo, 1975). Microbial degradation of TNG was first reported by Wendt et al. (1978) who found that the compound was readily biodegraded when batch or continuous techniques were used with activated sludge cultures. TNG was not a suitable carbon or nitrogen source; other organic nutrients such as glucose are needed. In shaker flasks containing 67 mg/liter TNG, glucose, and minimal salts, a 53.6% decrease in TNG concentration was observed after 5 days of incubation. Without glucose, only 3.1% loss was observed.

2,4-Dinitrotoluene (2,4-DNT)

Summary and Recommendations

Volatilization rate estimates show that volatilization may be an important fate process for 2,4-DNT that requires detailed study. Sediment adsorption may also be an important fate process, as indicated

by estimates of partition coefficients. This, too, requires further study. Photolysis studies also should be performed in view of the rapid photolysis of other ortho-nitrotoluene compounds. Biotransformation of 2,4-DNT is likely to occur in the environment, and detailed investigations of this fate are recommended.

Physical Properties

Solubility in Water

The solubility of 2,4-DNT at 22° C has been reported as 0.027 g/100 g of water, or 1.5×10^{-3} M (Desvergues, 1925). We found no other solubility data. The solubility should be remeasured at 20° C using the technique of Campbell (1934). That technique is described in Section II.

Vapor Pressure

Pella (1977) measured the vapor pressure of solid 2,4-DNT using a gas saturation method. The vapor pressure extrapolated from his data is 1.1×10^{-4} torr at 20° C.

Maksimov (1968) used 2,4-DNT near its boiling point. The extrapolated vapor pressure at 20° C is 5.1×10^{-3} torr, which should be a reasonable estimate of the vapor pressure of supercooled liquid 2,4-DNT.

Physical Transport

Volatilization Rate from Water

An estimated value of the Henry's law constant for 2,4-DNT is 3.4 torr M^{-1} . The estimated value of H_c suggests that the volatilization rate of 2,4-DNT is limited by gas-phase mass transport resistance. The estimated value of $(k_v^C)_{env}$ is $6.1 \times 10^{-4} \text{ hr}^{-1}$ and the half-life for volatilization is 47 days. The volatilization rate data of Spanggard et al. (1978) can be used to calculate a $(k_v^C)_{lab}$ value of $2.96 \times 10^{-3} \text{ hr}^{-1}$ and a $(k_g^W)_{lab}$ value of 3400 cm hr^{-1} . These values can be used to calculate $(k_v^C/k_g^W)_{lab}$ and $(k_v^C)_{env}$ using equation (A-28).

Then, from Eq. (A-30), (A-31), and (A-28),

$$\frac{k_v^C}{k_g^W} = \frac{2.96 \times 10^{-5}}{3400} = 8.66 \times 10^{-7} \text{ cm}^{-1}$$

$$\begin{aligned} \left(\frac{k_v^C}{k_g^W}\right)_{\text{env}} &= \left(\frac{k_v^C}{k_g^W}\right)_{\text{lab}} \frac{L_{\text{lab}}}{L_{\text{env}}} \left(\frac{k_g^W}{k_g^W}\right)_{\text{env}} \\ &= \frac{(8.66 \times 10^{-7})(7.8)(2100)}{(200)} \\ &= 7.1 \times 10^{-5} \text{ hr}^{-1} = 1.7 \times 10^{-3} \text{ day} \end{aligned}$$

and the estimated environmental half-life for volatilization is 410 days. This value is within an order of magnitude of the volatilization half-life estimated using the procedure described in the TNT section, which is excellent considering the approximations that were made.

These results suggest that volatilization of 2,4-DNT may be an important environmental fate and detailed volatilization rate studies are recommended.

Sorption on Soils and Sediments

No sediment or soil adsorption isotherm data for 2,4-DNT were found during the literature search. Based on the solubility of 2,4-DNT in water at 20°C and the correlation of K_{oc} and water solubility shown in Figure 1, the estimated K_{oc} is about 90. This value suggests that adsorption on sediments may not be a significant environmental fate. However, screening experiments are recommended.

Photolysis

Spangord et al. (1978) reported that 50% of the 2,4-DNT component of a TNT condensate water was lost after exposure to sunlight for about 5 days. A control solution maintained in the shade showed that the same amount of 2,4-DNT was lost in about 11 days. These data suggest that volatilization is competitive with direct photolysis of 2,4-DNT under the conditions of the experiment.

Burlinson and Glover (1977a) have reported that 2,4-DNT photolyzes more rapidly at higher pHs. Thus, photolysis at > 290 nm of 125-ppm 2,4-DNT solutions at pH 3.3 and 10.8 gave 44 and 92% reaction, respectively, after 5 hours of irradiation. In the same report, the authors summarized their previous work on identifying the 2,4-DNT photoproducts, accounting for 52% of the starting material lost. The products and their yields were--

- 2,4-Dinitrobenzaldehyde, 6%
- 2-Amino-4-nitrobenzaldehyde, 10%
- 2,2'-Carboxaldehyde-5,5'-dinitroazoxybenzene, 3%
- 2,4-Dinitrobenzoic acid, 7%
- 2-Amino-4-nitrobenzoic acid, 16%
- 2,2'-Carboxy-5,5'-dinitroazoxybenzene, 10%

Wettermark and Ricci (1963) and Wettermark et al. (1965) investigated the photolysis of 2,4-DNT in terms of the aci-quinoid intermediate formed during the flash photolysis of 2,4-DNT in a solvent of 1% ethanol in water. The transient intermediate in strong acid showed an absorption minimum at 400 nm and a peak absorption at 420 nm; in

strong base (0.1M NaOH), the minimum was at 450 nm and the maximum at 530 nm. The transition from the acid spectrum to base spectrum for the 2,4-DNT intermediate occurred at about pH 1, and the base spectrum was unchanged over the pH range of 2 to 13; the spectrum was also unchanged by the presence of oxygen or buffer salts. The spectrum of the nonirradiated 2,4-DNT was also found to be unchanged in the pH region of 0 to 13.

Wettermark et al. also reported that in NaOH solutions of pH 10 to 13 the first-order rate constant for decay of the base intermediate was 1.0 sec^{-1} . The rate of decay was affected by the buffer salt concentration, but the first-order rate constant for decay was also determined to be 1.0 sec^{-1} at pH 8.4 after extrapolation to infinite dilution for buffer salts. Below pH 5, the decay rate increased with lowered pH. Rate constants for neutralization of the basic transient intermediates were measured to be $7.4 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ for H^+ and $1.8 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ for reaction with water. The decay rate constants for both the acid and base intermediates were unaffected by oxygen at all pH levels except near pH 1 where the intermediate undergoes the acid/base change in spectrum.

The authors also reported that in addition to the transient spectrum, permanent visible absorptions appeared in the range 380 to 600 nm, with the extent of coloration from these photoproducts depending strongly on pH, buffer concentrations, and the presence of oxygen.

Sandus and Slagg (1972) reported a disappearance quantum yield of 1×10^{-3} for photolysis of 2,4-DNT in heptane solvent at 254 nm; the quantum yield was not affected by oxygen in solution.

Hydrolysis

No hydrolysis of 2,4-DNT is expected under environmental conditions.

Biodegradation

Chambers et al. (1963) reported evidence of degradation of 2,4-DNT with phenol-adapted bacteria and 100 mg/liter 2,4-DNT using respiratory

techniques. 2,4-DNT (100 mg/liter) was transformed by some fungi in basal medium with glucose (Parrish, 1977). Only 5 of 190 organisms tested transformed 2,4-DNT, compared with 183 for TNT.

McCormick et al. (1978) identified the products of transformation by a fungus Microsporium species grown in DNT, glucose, and basal medium. Those products were 2-amino-4-nitrotoluene (2-A-4-NT), 4-amino-2-nitrotoluene (4-A-2-NT), 2,2'-dinitro-4,4'-azoxytoluene, 4,4'-dinitro-2,2'-azoxytoluene, and 4-acetamido-2-nitrotoluene. 2,4-DNT was also reduced by hydrogen in the presence of an enzyme preparation from Veillonella alcalescens (McCormick et al., 1976).

No environmental fate study was performed.

CATEGORY II CHEMICALS

1,3-Dinitrobenzene (1,3-DNB)

Summary and Recommendations

Volatilization of 1,3-DNB is expected to be an important environmental fate process, so detailed studies are recommended. Sediment adsorption is not considered to be an important fate process; however, screening studies should be performed. Photochemical screening studies should be considered in natural waters because of a tailing of the uv absorption spectrum into the region above 200 nm. Biotransformation studies are necessary to determine microbial reduction rates of 1,3-DNB and the potential for occurrence of other biotransformations.

Physical Properties

Solubility in Water

Several researchers have measured the solubility of 1,3-DNB in water: Urbanski (1964) obtained 0.02 g/100 g of water (1.2×10^{-3} M) at 20° C; Leiga and Sarmousakis (1966) obtained 0.533 g liter⁻¹ (3.17×10^{-3} M) at 25° C; Kheifets et al. (1974) obtained 0.36 g liter⁻¹ (2.2×10^{-3} M) at 20° C. The data of Kheifets et al. are probably the best available.

Vapor Pressure

Maksimov (1968) measured the vapor pressure of liquid 1,3-DNB. His data, extrapolated to 20° C, give a vapor pressure of supercooled liquid 1,3-DNB of 3.9×10^{-3} torr.

Measures of the vapor pressure of solid 1,3-DNB have been reported (CA 59:12206f; 70:61315y). However, the units and some of the data are unclear, and we have not tried to analyze them because Maksimov's data are satisfactory for our purposes.

Physical Transport

Volatilization from Water

The estimated value of H_c for 1,3-DNB at 20° C is 1.8 torr M^{-1} . The estimated value of $(k_v^C)_{env}$, using equation (A-31), is 3.9×10^{-4} hr^{-1} and $(t_{1/2})_{env}$ is 73 days. The estimated value of $(k_v^C/k_g^W)_{lab}$, using data from Spanggard et al. (1978), is 6.4×10^{-7} cm^{-1} , which gives a value of $(k_v^C)_{env} = 5.2 \times 10^{-5}$ hr^{-1} and a half-life for volatilization of 550 days.

These results suggest that volatilization of 1,3-DNB may be an important environmental fate and detailed volatilization rate studies are recommended.

Sorption on Soil and Sediments

No sediment or soil adsorption isotherm data for 1,3-DNB were found during the literature search. Based on its .02% solubility in water and the correlation of K_{oc} and water solubility shown in Figure 1, the estimated value of K_{oc} is about 64. This suggests that adsorption on sediments may not be a significant environmental fate; however, screening experiments are recommended.

Photolysis

Spanggard et al. (1978) reported that 50% of the 1,3-DNB component of a TNT condensate water was lost after exposure to sunlight for about 12 days. A control solution maintained in the shade, however, showed that the same amount of 1,3-DNB was lost in about 14 days. The data suggest that volatilization is more rapid than direct photolysis of 1,3-DNB under the conditions of the experiment.

Sandus and Slagg (1972) measured the disappearance quantum yield for photolysis of 1,3-DNB in heptane at 254 nm; the quantum yield of 1×10^{-3} was independent of oxygen in solution. For reasons discussed under "Other Considerations," this information cannot be applied in predicting an environmental photolysis rate for 1,3-DNB at this time.

Several research groups have studied the interaction of chlorophyll and 1,3-DNB in stabilizing chlorophyll toward photolysis. As discussed under "Other Considerations," research has not revealed how this chemistry may be important in phototransformations of nitroaromatics (in this case, 1,3-DNB) in aquatic environments. The following information on the chlorophyll-1,3-DNB chemistry, however, indicates the possible existence of the charge transfer complex or radical anion species of 1,3-DNB, which may result in 1,3-DNB transformations in aqueous environments if less simple (i.e., irreversible) reactions were to occur.

Vrbaski (1950) found that the photofading of chlorophyll is retarded by the presence of 1,3-DNB and suggested that a chlorophyll-1,3-DNB complex is responsible for the stabilization. A more mechanistic explanation for this apparent stabilization is provided by Chernyuk and Dilung (1965), who found that when chlorophyll in an ethanol-glycerine mixture containing 1,3-DNB was irradiated at -75°C the chlorophyll was bleached with the appearance of a new absorption band at 470 to 570 nm. This low-temperature product gave a complex epr signal and was believed to be due to an ion-radical pair formed by transfer of an electron from chlorophyll to 1,3-DNB. The transfer was mostly reversed in the dark in fluid medium, although a small amount of chlorophyll was oxidized irreversibly.

Ivnitskaya et al. (1968) reported that the photoreaction of chlorophyll, 1,3-DNB and the leuco base of malachite green proceeds by oxidation of the photoexcited chlorophyll by 1,3-DNB, with subsequent reduction and oxidation of the oxidized chlorophyll and reduced

1,3-DNB species, respectively, in a more complex mechanism. Such reversible oxidation-reduction sequence(s) should serve to slow the photofading rate of chlorophyll.

Hydrolysis

Hydrolysis of 1,3-DNB is not expected to occur under environmental conditions.

Biodegradation

Cartwright and Cain (1959) reported that an extract of Nocardia erythropolis reduced 1,3-DNB to corresponding arylamines. In a respiratory study with phenol-adapted bacteria, Chambers et al. (1963) showed that oxygen consumption was not significantly higher than endogenous respiration with 1,3-DNB or with 1,3,5-TNB, indicating that little or no biodegradation of these chemicals occurred. Alexander and Lustigman (1966) reported that 1,3-DNB is resistant to attack by soil microorganisms as measured by loss of uv absorption in medium with 5 µg/ml 1,3-DNB.

Bringmann and Kuehn (1971) reported that 1,3-DNB and 1,3,5-TNB, both at an initial concentration of 136 mg/liter, were reduced 100 and 98%, respectively, in a two-stage model wastewater purifier.

2,6-DNT, 1,3-DNB, and 1,3,5-TNB were reduced by hydrogen with an enzyme preparation of V. alkalescences (McCormick et al., 1976).

Further studies are needed to determine the importance of biotransformation for 1,3-DNB.

1,3,5-Trinitrobenzene (TNB)

Summary and Recommendations

Volatilization and sediment adsorption are expected to be significant for 1,3,5-TNB, and detailed investigations are recommended. Since uv absorption tailing into the region above 300 nm occurs, photochemical screening studies should be performed. Also, photolysis screening studies should be performed in the presence of a natural water. Biological studies of 1,3,5-TNB are needed to delineate this fate process.

Physical Properties

Solubility in Water

The solubility of 1,3,5-TNB has been measured by several workers. Urbanski (1964) reported a solubility of 0.03 g/100 g of water (1.4×10^{-4} M) at 17° C. Desvergnès (1925) found 0.0278 g/100 g of water at 15° C; other measurements at 50 and 100° C are also reported. The extrapolated solubility of 1,3,5-TNB at 20° C is 0.034 g/100 g of water (1.6×10^{-4} M).

Vapor Pressure

Maksimov (1968) measured the heat of vaporization, ΔH_v , of 1,3,5-TNB as 17.5 kcal mole⁻¹. That value can be used to calculate the vapor pressure using the Clausius-Clapeyron equation. Using a boiling temperature of 315° C at 760 torr, the vapor pressure of the supercooled 1,3,5-TNB liquid is approximately 2.2×10^{-6} torr at 20° C.

Nitta et al. (1950) measured the vapor pressure of 1,3,5-TNB over a temperature range of 80 to 132° C using a modified Knudsen technique. Those data can be extrapolated to 20° C, giving values of 3.2×10^{-6} torr (solid) and 5.1×10^{-6} torr (liquid). The agreement between the data of Maksimov and Nitta et al. is poor.

Physical Transport

Volatilization Rate from Water

The estimated value of H_c for 1,3,5-TNB using the more recent data of Maksimov (1968) is 1.3 torr M⁻¹, which gives an estimated $(k_v^C)_{env}$ using Equation (A-31), of 2.2×10^{-4} hr⁻¹ and $(t_{1/2})_{env} = 130$ days. These estimates suggest that volatilization of 1,3,5-TNB may be significant and detailed volatilization rate measurements are recommended.

Sorption on Soils and Sediments

No sediment or soil adsorption isotherm data for 1,3,5-TNB were found during the literature search. Based on the solubility in water at 20° C and the correlation of K_{oc} and water solubility shown

in Figure 1, the estimated value of K_{oc} is 520. This value suggests that adsorption on sediments may be a significant environmental fate. Therefore, detailed adsorption isotherm experiments are recommended.

Photolysis

In a study of the stability of TNT photoproducts, Burlinson et al. (1973) reported that 1,3,5-TNB in aqueous solution was unchanged after irradiation for 6 hours with a Hg arc (presumably with a borosilicate filter to exclude light > 290 nm). The authors apparently did not pursue these studies further.

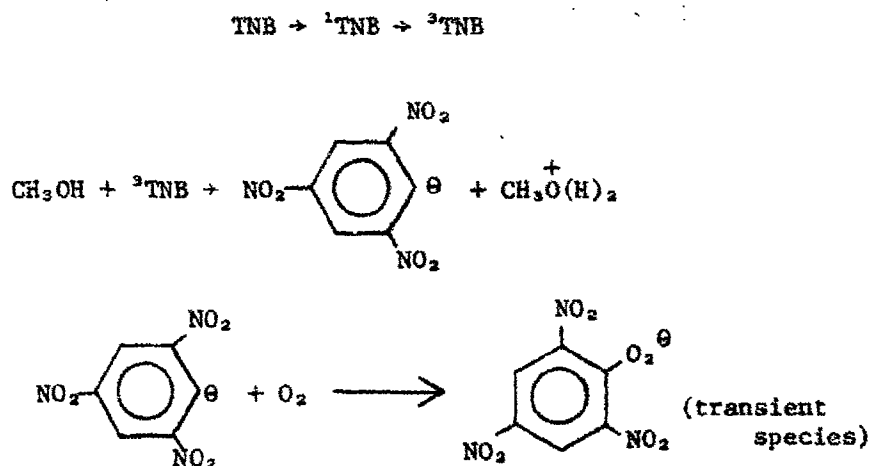
Other studies that provide information on the chemistry of TNB but that have no obvious application to environmental aquatic systems have been reported. Gold and Rochester (1960) reported that irradiation of a solution of 10^{-4} 1,3,5-TNB in 0.5 N NaOH with a 150-watt incandescent bulb caused the colored mixture (presumably σ -complex) to fade 50 times faster than an identical solution maintained in the dark. Yields of nitrite and 3,5-dinitrophenol of 95% were obtained in the irradiated solution. In the dark reaction, small amounts of ammonia and picric acid were found in addition to nitrite and 3,5-dinitrophenol. In the irradiated solution, the rate of nitrite formation was equal to the rate of fading of the complex; but in the dark, the nitrite production lagged behind the fading process.

Letellier and Gaboriaud (1975) reported that the σ -complex of OH^- and 1,3,5-TNB ultimately gave picric acid as a product. Abe (1961) also found that the colored complex of 10^{-5} M 1,3,5-TNB in a solvent of 4% water in acetone containing 0.04 M NaOH faded within hours and that the solutions then became turbid. The information in these papers is insufficient to make comparisons on the similarities or differences in the chemical processes, however.

Stenberg and Holtzer (1964) found that 1,3,5-TNB in ethanol solvent irradiated for 36 hours with a Hg lamp/quartz well system gave up to 28% yields 3,3',5,5'-tetranitroazoxybenzene. Stenberg et al. (1977) cite references in which photoreduction of nitrobenzene

proceeds by triplet state abstraction of hydrogen atoms from amine, alcohol, ether, and hydrocarbon solvents. In that paper, the authors report that photolysis of 1,3,5-TNB in 1-propanol at 366 nm gave reaction quantum yields that decreased from 0.071 to 0.015 with longer irradiation; nitrobenzene reduction quantum yields decreased from 0.067 to 0.010 in the same system. Stenberg et al. suggested that a nitroxide formed during photolysis was responsible for quenching the triplet state nitroaromatic and hence for the lowered quantum yields.

Capellos and Suryanarayanan (1972) reported flash photolysis studies on 1,3,5-TNB in air-saturated alcohol solvents, with a transient species having λ_{max} at 430 and 500 nm. They state that the photolysis mechanism requires a polar solvent with proton affinity as follows.



In oxygen-free methanol, a permanent product is formed, which the authors believe is a methoxide/TNB complex.

The electrophilic nature of 1,3,5-TNB has been described. The interaction of nitroaromatics in the photostabilization of chlorophyll was discussed in the preceding section on 1,3-DNB. Larry (1967) studied the charge transfer complexation of 1,3,5-TNB with chlorophyll. Kawai et al. (1969) found that flash photolysis of *p*-dimethoxybenzene

(DMB) in oxygen-free acetonitrile in the presence of 1,3,5-TNB produces DMB cation radical via electron transfer to 1,3,5-TNB. In this system, the radical pair disproportionates back to starting material. Although the ability of 1,3,5-TNB to serve as an electrophilic agent is well established--as would be expected for such a nitro-substituted molecule--the significance of its electron-accepting character in its environmental chemistry is yet to be determined.

Hydrolysis

Hydrolysis of 1,3,5-TNB is not expected to occur under environmental conditions.

Biodegradation

The biodegradation of 1,3,5-TNB is described in the preceding section on 1,3-DNB (see page 36).

2,6-Dinitrotoluene (2,6-DNT)

Summary and Recommendations

Volatilization and sediment adsorption are expected to be significant fate processes for 2,6-DNT and are recommended for detailed study. Photolysis will be a rapid process, and in-depth studies of that process are also recommended. The effect of pH on photolysis rates should also be investigated. No evidence was found for the biotransformation of 2,6-DNT. However, by analogy to other DNT isomers, biological screening studies are recommended.

Physical Properties

Solubility in Water

No solubility data for 2,6-DNT were found. Measuring its solubility in water at 20° C is recommended using the technique described in Section II. A reasonable estimate, based on the solubility of 2,4-DNT, is 1×10^{-3} M.

Vapor Pressure

Pella (1977) reported that the vapor pressure of solid 2,6-DNT at 20° C is 3.5×10^{-6} torr, as measured by a gas saturation technique.

Maksimov (1968) reported a vapor pressure that can be used to estimate the vapor pressure of supercooled 2,6-DNT. His data give a vapor pressure of 0.018 torr at 20° C. This estimate seems high compared with the value for solid 2,6-DNT measured by Pella.

Physical Transport

Volatilization Rate from Water

The value of H_c for 2,6-DNT, which was estimated from the estimated solubility of 1×10^{-3} M and the vapor pressure reported by Maksimov (1968) of 0.018 torr, is 18 torr M^{-1} . Then, the estimated value of $(k_v^C)_{env}$, using Equation (A-31), is $3.2 \times 10^{-3} \text{ hr}^{-1}$ and $(t_{1/2})_{env} = 9$ days. Using the data reported by Spanggord et al. (1968), $(k_v^C/k_g^W)_{lab} = 2.5 \times 10^{-6} \text{ cm}^{-1}$, which suggests that $(k_v^C)_{env}$ is 4.8×10^{-3} day and $(t_{1/2})_{env} = 140$ days. These estimates suggest that volatilization may be a significant environmental fate and detailed volatilization studies are recommended.

Sorption on Soils and Sediments

No sediment or soil adsorption isotherm data for 2,6-DNT were found during the literature search. Based on its .02% solubility in water and the correlation of K_{oc} and water solubility shown in Figure 1, the estimated value of K_{oc} is about 100. This value suggests that adsorption on sediments may be a significant environmental fate. Hence, detailed adsorption isotherm experiments are recommended.

Photolysis

Spanggord et al. (1978) reported that 50% of the 2,6-DNT component of a TNT condensate water was lost after exposure to sunlight for about 1 day. A control solution maintained in the shade showed that the same amount of 2,6-DNT was lost in about 5 days. This suggests that volatilization is slower than direct photolysis of 2,6-DNT under the conditions of the experiment.

Burlinson and Glover (1977c) have reported that a 150-ppm 2,6-DNT solution contained only 0.2 ppm 2,6-DNT after exposure to sunlight for 5 days. The solution contained at least 40 products (by hplc) and 30 to 40% polymeric material. Some products identified by hplc were azoxy and azo benzene structures with methyl and nitro substituents and their derivatives (i.e., aldehyde, acid and nitroso, oxime groups, respectively). Subsequently, Burlinson and Glover (1977b) further reported that 2,6-DNT is photolyzed more rapidly with increased pH; 4, 18, and 31% losses of 2,6-DNT occurred when 100-ppm solutions at pH 4.6, 6.7, and 10.8 were irradiated for 5 minutes with a borosilicate-filtered Hg lamp.

Langmuir et al. (1969) studied the flash photolysis of 2,6-DNT in the same system as described previously. The aci-quinoid isomer of 2,6-DNT was determined to have a pK_a of 1.8, with a rate constant for tautomerization to the nitro form of $2 \times 10^{-3} \text{ sec}^{-1}$ at 30°C ; the latter rate constant corresponds to a half-life of $3.5 \times 10^{-4} \text{ sec}$. Langmuir et al. also determined that above pH 6 a limiting rate constant of 0.95 sec^{-1} is attained for fading of the anion. The rate constants for protonation of the anion by H_2O and H^+ were measured as $1.6 \times 10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$ and $1 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$, respectively.

Hydrolysis

2,6-DNT is not expected to hydrolyze under environmental conditions.

Biodegradation

No studies were found on the biodegradation of 2,6-DNT, except by enzyme preparation (see "Biodegradation" section for 1,3-DNB). By analogy to 2,4-DNT, biodegradation will probably occur in the environment.

2,3,6-Trinitrotoluene (2,3,6-TNT)

No reports were found on the environmental fate of 2,3,6-TNT. Therefore, all the screening tests are recommended for this compound.

CATEGORY III CHEMICALS

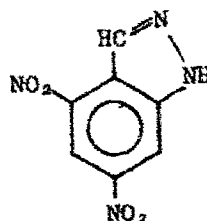
2-Amino-4,6-Dinitrotoluene (2-A-4,6-DNT)

Summary and Recommendations

No publications were found on the environmental fate of 2-A-4,6-DNT. Therefore, all screening studies should be performed to identify dominant fate processes.

Photolysis

Burlinson and Glover (1977b) have reported that photolysis of 50 ppm 2-A-4,6-DNT at > 290 nm in an unbuffered aqueous solution produced about 70% loss in 7 hours. Six products were evident by tic analysis of the CH₂Cl₂ extract, but the largest product yield was only 2%. The only product identified from the photolysis was 4,6-dinitroindazole.



Biodegradation

2-A-4,6-DNT was identified as a metabolite of 2,4,6-TNT (Won et al., 1974; McCormick et al., 1976; Hoffsommer et al., 1978), and 2-A-4,6-DNT was further reduced (Hoffsommer 1978). In a batch study, 13 ppm 2-A-4,6-DNT was lost after 3 days of incubation with sludge microbes. 2,4-Diamino-6-nitrotoluene and 2,6-diamino-4-nitrotoluene were produced. No other studies have been reported regarding biotransformation of 2-A-4,6-DNT.

3,4-Dinitrotoluene (3,4-DNT)

Summary and Recommendations

No literature on the environmental fate of 3,4-DNT was found. Solubility and volatilization rate studies and detailed adsorption isotherm experiments are recommended. Photolysis screening studies in natural water should also be performed.

Volatilization Rate from Water

No solubility or vapor pressure data for 3,4-DNT were found. The volatilization rate data of Spanggord et al. (1978) can be used to estimate $(k_v/k_g)_{lab} = 6.9 \times 10^{-7} \text{ cm}^{-1}$, $(k_v)_{env} = 1.4 \times 10^{-3} \text{ day}^{-1}$, and $(t_{1/2})_{env} = 500 \text{ days}$. These estimates suggest that volatilization of 3,4-DNT may be a significant environmental fate and detailed volatilization studies are recommended.

Photolysis

Spanggord et al. (1978) reported that 50% of the 3,4-DNT component of a TNT condensate water was lost after exposure to sunlight for about 10 days. A control solution maintained in the shade, however, showed that the same amount of 3,4-DNT was lost in about 13 days. This suggests that volatilization is more rapid than direct photolysis of 3,4-DNT under the conditions of the experiment.

5-Amino-2,4-Dinitrotoluene (5-A-2,4-DNT)

Summary and Recommendations

No literature on the environmental fate of 5-A-2,4-DNT was found. Performance of all screening studies is recommended to identify dominant fate processes.

Volatilization and Photolysis

Spanggord et al. (1978) reported that 50% of the 5-A-2,4-DNT component of a TNT condensate water was lost after exposure to sunlight for about 16 days. A control solution maintained in the shade showed that only 4% was lost in about 17 days. This suggests that volatilization is much slower than direct photolysis of 5-A-2,4-DNT under the conditions of the experiment.

The estimated value of $(k_{\text{deg}}^{\text{C/W}})_{\text{lab}}$ is $1.2 \times 10^{-7} \text{ cm}^{-1}$, using the data reported in Spanggard et al. (1978). This suggests that the half-life of 5-A-2,4-DNT would be 2800 days, and volatilization studies are not recommended.

OTHER CONSIDERATIONS

In the literature, a number of processes are described, related mainly to the nitroaromatic compounds, that may occur under selected environmental conditions. These include the processes that depend on the acidity of nitroaromatics, π - and σ -complexation of nitroaromatics including charge-transfer complexes, photoreduction, reduction in the presence of metal ions, and oxidation. Should these processes occur to any degree in the environment, the rate and equilibrium constants governing them would need to be incorporated into the total modeling expression.

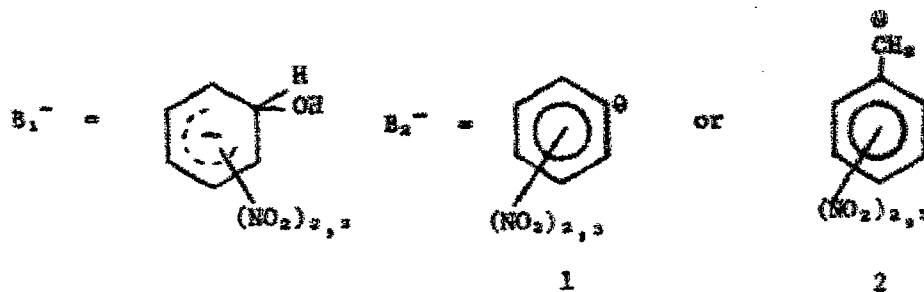
The following sections describe these processes and their potential environmental significance.

The Nature of the Acidity of Nitroaromatics

Information on several nitroaromatics containing two or three nitro group substituents indicates that the acidity of these compounds is due to the Lewis acid character of the aromatic ring (Scheme 1) rather than to the more familiar proton donor mechanism as defined by the Lowry-Bronsted acid-base theory. In the chemical equations and equilibria expressions for the two processes, Ar is the neutral nitroaromatic species; the anionic species B_1^- and B_2^- have the general structures illustrated below.



Scheme 1



Both B_1^- and structure 2 of B_2^- are stabilized by resonance when electron-withdrawing substituents such as nitro groups are located ortho or para to the $-OH$ and $-CH_2^-$ groups on the respective anions. Stable anions such as B_1^- formed by reaction of nitroaromatics with nucleophiles are known and are called σ -complexes or Meisenheimer complexes.

In basic aqueous solution, the structures B_1^- and B_2^- are indistinguishable insofar as the mathematical treatment of the equilibrium process is concerned, and the equilibrium expressions can then be defined in terms of a general anionic intermediate B^-

$$K_a = \frac{(B^-)(H^+)}{(Ar)} \qquad K_{eq} = \frac{(B^-)}{(Ar)(OH^-)}$$

Using these equilibria expressions and the autoprotolysis relationship, $(H^+)(OH^-) = K_w$, the relationship between the apparent acid dissociation constant, K_a , and the equilibrium constant for σ -complex formation, K_{eq} , can be shown to be

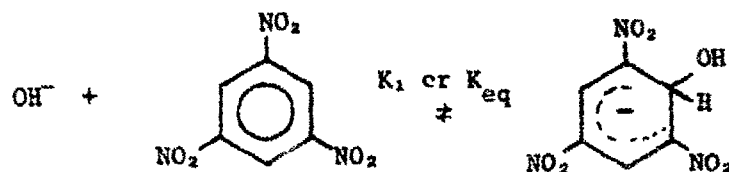
$$K_a = K_w K_{eq}$$

Thus, the acidity of the nitroaromatics can be evaluated in terms of conventional acidity or as the hydroxyl ion complexation reaction.

Schaal (1954) reported the pK values tabulated below for some polynitroaromatic compounds.

<u>Nitroaromatic Compound</u>	<u>pK₁ at 25° C</u>
TNB	14.4 (pK ₂ , 18.0)
1,3-DNB	16.8
2,4-DNT	17.1
2,6-DNT	> 19
TNT	14.4 (pK ₂ , 17.6)

He did not specify which TNB or TNT isomers were studied, but presumably they were 1,3,5-TNB and 2,4,6-TNT. Schaal also noted that at least one proton must be ortho to two nitro groups for a pK < 19. Schaal suggested that the acidity of the nitroaromatic was the result of OH⁻ addition to the aromatic ring as shown below for TNB. In support of this mechanism, Bernasconi (1970) measured the equilibrium constant K_{eq} for the reaction of TNB with OH⁻ as 3.73 M⁻¹ at 25° C;



when this is recalculated according to the acidity formalism of Schaal, the pK₁ is 13.4. In fair agreement with that of Bernasconi, the TNB + OH⁻ ⇌ (TNB-OH⁻) equilibrium constant measured by Abe (1960) was 2.7 M⁻¹ at 25° C.

In accord with the mechanism of reversible OH⁻ addition rather than reversible H⁺ removal from TNB, Gold and Rochester (1960) and Ketelaar et al. (1954) found no H-D exchange when 1,3,5-TNB was placed in D₂O at 0.5 N and 8 N NaOH, respectively. The difference between use of water and ethanol as solvent for measuring the acidity of TNT is difficult to assess. Nevertheless, the data presented by

Caldin (1959) indicate that in an ethanol/ethoxide system, proton transfer from the methyl group is about two orders of magnitude slower than the rate of ethoxide addition to the TNT aromatic ring at 25° C.

Although this information indicates that nitroaromatics in aqueous solution will not be ionized in the environmental pH region of about 3 to 10, Letellier and Gaboriaud (1975) reported almost complete ionization of TNT in micellar solution (using hexadecyltrimethylammonium bromide, CTAB) with 10^{-3} N NaOH. The relevance of such a micellar effect on the environmental chemistry of nitroaromatics is not known.

Charge Transfer Complexes with Nitroaromatics

Zeichmann (1972) has discussed the interaction of humic substances with various chemicals. He cites 1,3,5-TNB as an electron acceptor that may form charge transfer complexes with humic substances serving as the electron donor. Chlorophyll, present in both terrestrial and aquatic systems, also forms charge transfer complexes with 1,3,5-TNB (Larry, 1967). No information has been found, however, that is useful for assessing whether these complexes occur at the dilute concentrations of nitroaromatics and of natural substances that are expected in aquatic systems or whether the formation of such complexes alters the environmental chemistry of the nitroaromatic relative to its chemistry in less eutrophic waters.

Regarding the charge transfer complex between nitroaromatics and chlorophyll, the role of nitroaromatics in stabilizing the photofading of chlorophyll has been attributed to the electron-acceptor properties of the nitroaromatic system; this chemistry is described in the section on 1,3-DNB. Vrbaski (1950) suggests that the stabilization is due to a complex between the nitroaromatic and chlorophyll. The stabilization mechanisms suggested by other researchers do not require complexation but only a net reversible electron transfer between chlorophyll and the nitroaromatic. No information is available to

determine whether irreversible electron transfer from chlorophyll or other natural substances may produce transformations of nitroaromatics in aquatic environments. The irreversible formation of such a reactive radical anion would probably produce some reaction of the nitroaromatic. Charge transfer complexation of nitroaromatics with natural substances requires investigation. If the nitroaromatic complexes are formed in the aquatic environment, their uv-visible absorption spectra would be different and therefore the photochemical transformation rates would be different than those for nitroaromatic in pure water. The π -complexed nitroaromatic may also alter the relative importance of the various fate processes (i.e., oxidation, sorption, photolysis) than for the nitroaromatic alone.

σ -Complexes of Nitroaromatics

Sasaki (1973) has measured the kinetics and equilibrium constants for sulfite addition to 1,3,5-TNB at 25° C. $\text{SO}_3^{2-} + \text{TNB} \xrightleftharpoons[k_{-1}]{k_1} (\text{TNB-SO}_3^{2-})^-$. The forward reaction has a rate constant, k_1 , of $(3.70 \pm 0.22) \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$, with an equilibrium constant, K , of $(3.22 \pm 0.45) \times 10^3 \text{ M}^{-1}$. These values may be compared with the data for OH^- addition to 1,3,5-TNB reported by Bernasconi (1970): $k_1 = 37.5 \pm 1.8 \text{ M}^{-1} \text{ sec}^{-1}$ and $K = 3.73 \pm 0.37 \text{ M}^{-1}$. The σ -complexes for acetonitrile anion/2,4-DNT and 1,3,5-TNB (Gitlis et al., 1975) and for cyanide ion/1,3,5-TNB (Gan and Norris, 1974a,b) have also been described. Because the high concentrations of strong nucleophiles required for these complexes do not exist in natural aquatic environments, formation of σ -complexes most likely will not be an important influence on the environmental fate of nitroaromatics.

Photoreduction of Nitroaromatics

Several studies on the photoreduction of nitroaromatics have been reported. These reactions appear to proceed by a hydrogen atom transfer from a donor molecule to the $n-\pi^*$ triplet state of the nitroaromatic. Sandus and Slagg (1972) have measured the disappearance quantum yields for photolysis of several nitroaromatic compounds. These data

are useful only for determining the relative reactivity of these compounds insofar as environmental photolysis evaluations are concerned because the photolyses were carried out in heptane solvent and at 254 nm. Some of the disappearance quantum yields reported are tabulated below.

<u>Nitroaromatic Compound</u>	<u>Disappearance Quantum Yield $\times 10^3$</u>
Nitrobenzene	3
o-Nitrotoluene	4
m-Nitrotoluene	2
m-Dinitrobenzene (1,3-DNB)	1
2,4-Dinitrotoluene (2,4-DNT)	1
2,4,6-TNT (in cyclohexane)	1

Sandus and Slagg also found that oxygen did not affect the quantum yields. The products of the reactions were suggested to be nitrosoaromatics, with a nitrophenol also suggested to be a photoproduct of nitrobenzene.

Hurley and Testa (1966) reported the photolysis of nitrobenzene at 366 nm in isopropyl alcohol solvent. They claim that the photolysis proceeds through the triplet state of nitrobenzene, which abstracts a hydrogen atom from the solvent to ultimately form phenylhydroxylamine. This product is then oxidized in the presence of air to give nitrosobenzene. Reaction of nitrosobenzene and phenylhydroxylamine produces azoxybenzene. The latter product was quantitatively formed when both nitroso and hydroxylamine compounds were present at greater than 2×10^{-3} M, but in dilute solutions at 10^{-3} M only nitrosobenzene, and not azoxybenzene, was formed. The quantum yield for the disappearance of nitrobenzene measured in this system was $\sim 1 \times 10^{-2}$. However, Stenberg et al. (1977) subsequently reported that the quantum yields for photolysis of nitrobenzene and 1,3,5-TNB in isopropyl alcohol decreased with increased irradiation time. They suggested that formation of a nitroxide radical during photolysis quenched the triplet state of nitrobenzene, decreasing the quantum yield.

The photoreduction mechanism described does explain formation of nitrosoaromatics and azoxy benzene compounds, but the environmental relevance of such processes is difficult to evaluate. Unlike isopropyl alcohol or even heptane, water is a very poor hydrogen atom donor in radical abstraction reactions. Furthermore, although some evidence suggests that naturally occurring substances possess efficient radical-trapping properties, the ability of these substances to serve as hydrogen atom donors in reduction processes has not been determined.

Reduction of Nitroaromatics by Metal Ion

The facile reduction of nitroaromatics to intermediate or fully reduced forms by a variety of reducing agents, ranging from basic glucose to strongly acidic stannous ion, prompts consideration of possible environmental agents that might also effect their reduction by electron transfer.

A mode of electron transfer in the environment is found in sediments in the form of simple or complexed Fe^{2+} . Electron transfer from Fe^{2+} can effect cleavage of C-Cl bonds, probably via radical intermediates.



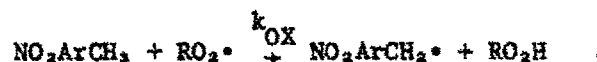
This process can also be envisioned as a loss mechanism for the easily reduced nitroaromatics. Examples of this process for chloro compounds are found in reduction of DDT in soil (Glass, 1972), reduction of toxaphene in estuarine sediments (Williams and Bidleman, 1977), and by Fe protoporphyrin (Khalifa, Holmstead and Castro, 1973).

Although the high electronegativity of nitroaromatics suggests that this class of structures would be susceptible to electron transfer from Fe^{2+} in some forms and thus would suffer partial reduction, no published reports on such studies have been found. (In circumstances where nitroaromatics are rapidly lost by photolysis or by some other process, reduction by sediment-bound Fe^{2+} probably would not compete, especially in view of the generally low sorption equilibrium

constants exhibited by most nitroaromatics.) Nonetheless, a brief examination of this possible loss process seems warranted because virtually nothing is known about the possible range of rate constants and the fact that nitroaromatics in water may be exposed to large amounts of Fe^{2+} sediments.

Oxidation of Nitroaromatics

Nitroaromatics in aquatic systems may be oxidized by a direct photoprocess involving reaction of some intermediate quinoid or diradical form with oxygen, in which case the photochemistry (quantum yield and spectrum) will control the rate of the process. Nonphotochemical oxidation may also occur via reaction only with free radicals such as RO_2^\bullet or RO^\bullet ; singlet oxygen probably is too selective to exhibit any reactivity toward nitroaromatics. The literature records only one or two citations to quantitative studies of oxidation of nitroaromatics via the radical process



The rate constant k_{OX} for nitrotoluene is about half that for toluene at 30° C ($k_{\text{OX}} = 0.012 \text{ M}^{-1} \text{ s}^{-1}$) and indicates that additional nitro groups will probably deactivate the ring further. Since toluene reacts with RO_2^\bullet with a half-life in aquatic systems of 2×10^3 years, and polynitroaromatics should be less reactive, we conclude that free radical oxidation of nitroaromatics will not be an important environmental fate process; hence, no studies are needed.

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Appendix A

PREDICTION OF VOLATILIZATION RATES

Appendix

PREDICTION OF VOLATILIZATION RATES

Two-Film Theory

The two-film mass transport theory is the simplest mathematical description of the evaporation process from a liquid phase to a gas phase. This theory was originally developed by Whitman (1923) and was recently applied to the problem of the evaporation rate of chemicals from water by Liss and Slater (1974), Mackay and Leinonen (1975), Smith et al. (1977), and Smith and Bomberger (1978). The basic concept is that there are two boundary layer regions near the gas-liquid interfacial surface: the liquid phase boundary layer and the gas phase boundary layer.

The transport of a substance through a boundary layer is assumed to be by molecular diffusion, because the fluid flow is laminar. The diffusion process can be described by Fick's law in one dimension, where the flux of the substance, N (moles $\text{cm}^{-2} \text{sec}^{-1}$) is

$$N = -D \frac{\partial C}{\partial z} \quad (\text{A-1})$$

where D is the diffusion coefficient, C is the concentration of the chemical, and z is the vertical distance. If the concentration gradient $\partial C / \partial z$ is constant within the boundary layer, equation (A-1) can be rewritten

$$N = k \Delta C \quad (\text{A-2})$$

The mass transport coefficient k has the units of velocity (cm sec^{-1}) and is

$$k = D / \delta \quad (\text{A-3})$$

where δ is the boundary layer thickness. This equation is correct for both the gas and liquid phase. In the development below, the subscripts g and l refer to the gas and liquid phases, respectively.

The flux through the liquid phase boundary layer, N_L , is

$$N_L = k_L (C_W - C_{sl}) \quad (A-4)$$

where k_L is the mass transport coefficient of the chemical in the liquid phase, C_W is the concentration of the chemical in the bulk liquid phase, and C_{sl} is the concentration of the chemical in the liquid phase at the gas-liquid interface (moles cm^{-3}).

The flux through the gas phase boundary layer, N_g , is

$$N_g = k_g (C_{sg} - C_g) \quad (A-5)$$

where k_g is the gas phase mass transport coefficient, C_{sg} is the gas phase concentration of C at the gas-liquid interface, and C_g is the concentration of the chemical in the bulk gas phase.

For any substance, the flux through each boundary layer must be equal to the overall flux from the bulk liquid to the bulk gas phase, N . Henry's law relates C_{sg} and C_{sl}

$$C_{sg} = H C_{sl} \quad (A-6)$$

where H is the Henry's law constant (unitless, as defined here). Then, substituting equations (A-5) and (A-6) into (A-4), we obtain

$$N = k_L \left[C_W - \frac{1}{H} \left(\frac{N}{k_g} + C_g \right) \right] \quad (A-7)$$

Collecting terms in N and solving for N gives

$$N = \left(\frac{1}{k_L} + \frac{1}{H k_g} \right)^{-1} \left(C_W - \frac{C_g}{H} \right) \quad (A-8)$$

In the laboratory, $C_g \approx 0$. The volatilization rate of the chemical, R_v , is

$$R_v = N/L = k_v C_L \quad (A-9)$$

where L is the depth of the bulk liquid phase (cm), and

$$k_v = \frac{1}{L} \left(\frac{1}{k_l} + \frac{1}{H k_g} \right)^{-1} \quad (\text{A-10})$$

Henry's law can also be written as

$$P^C = H_c C_l \quad (\text{A-11})$$

where P^C is the vapor pressure of C above the solution, and C_l is the concentration of the chemical in solution (in moles liter⁻¹ = M). The Henry's law constant, H_c , is in units of torr M⁻¹. From the ideal gas equation,

$$P^C = RT C_g \quad (\text{A-12})$$

where R is the gas constant and T is the temperature. Substituting equation (A-12) in (A-11) and comparing the result with the form of Henry's law as expressed in equation (A-6),

$$H_c = RT H \quad (\text{A-13})$$

Making the conversion to H_c and C_l in M, equations (A-8) and (A-10) become

$$N = \left(\frac{1}{k_l} + \frac{RT}{H_c k_g} \right)^{-1} \left(C_l - \frac{P^C}{H_c} \right) \quad (\text{A-14})$$

and

$$k_v = \frac{1}{L} \left(\frac{1}{k_l} + \frac{RT}{H_c k_g} \right)^{-1} \quad (\text{A-15})$$

When the liquid phase is water and the gas phase is air, typical values of k_l and k_g for molecules are 10-50 cm hr⁻¹ and 1000-4000 cm hr⁻¹ (Liss and Slater, 1974). The value of RT is 18,300 torr M⁻¹ at 20°C. Therefore, if $H_c \sim 10^3$ torr M⁻¹, the second term in equation (A-15) is small and k_v will be determined by the value of k_l . This means that the

rate of mass transport (volatilization) is limited by diffusion through the liquid phase boundary layer. We have called compounds that fit within this class "high volatility compounds." Similarly, if $H_c < 10 \text{ torr M}^{-1}$, the second term in equation (A-15) dominates and the rate of volatilization is limited by mass transport in the gas phase. We have called these "low volatility compounds." If H_c is between 10 and 1000 torr M^{-1} , both terms are important. We have called these "intermediate volatility compounds."

Estimation of the Henry's Law Constant, H_c

If a value of H_c can be estimated, then, as shown in the following sections, the volatilization rate of a chemical can be estimated. When the liquid phase is water, the value of H_c for a liquid (at 20°C) can be measured (Mackay et al. 1979) or estimated from the vapor pressure and the solubility in water using

$$H_c = P^C / C_{\text{sat}} \quad (\text{A-16})$$

where P^C is the vapor pressure of pure liquid C, and C_{sat} is the solubility of pure C in water (M) at 20°C .

If the vapor pressure of the liquid is available only at some temperature other than 20°C , the integrated form of the Clausius-Clapeyron equation

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{RT} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{\Delta H_v}{1.937} \left(\frac{1}{T_2} - \frac{1}{293} \right) \quad (\text{A-17})$$

can be used to estimate the vapor pressure at $T_1 = 20^\circ\text{C}$; P_2 is the vapor pressure at temperature T_2 (K), P_1 is the vapor pressure at 293 K, and ΔH_v is the heat of vaporization (cal mole^{-1}). Because this extrapolation may not be accurate over a wide temperature range, the vapor pressure should be measured at 20°C , if possible. Methods for measuring vapor pressure (Thomson and Dovslin, 1971) and solubility (Mader and Grady, 1971) have been reviewed.

If the chemical is a solid at 20°C, the vapor pressure that should be used in equation (A-17) is the vapor pressure of the supercooled liquid (Prausnitz, 1969; Mackay et al., 1979), P_{vsL}^C , which can be calculated using

$$\ln \frac{P_{vsL}^C}{P_{vs}^C} \approx \frac{\Delta H_f}{RT} \left(1 - \frac{T}{T_m} \right) \quad (A-18)$$

where P_{vs}^C is the vapor pressure of solid C at temperature T (293 K), ΔH_f is the heat of fusion of C (cal mole⁻¹), R is the gas constant (1.987 cal K⁻¹ mole⁻¹), and T_m is the melting point (K).^{*} Then, H_c for a solid at 20°C is

$$H_c = \left[P_{vs}^C \exp \frac{\Delta H_f}{582.2} \left(1 - \frac{293}{T_m} \right) \right] / C_{sat} \quad (A-19)$$

Low Volatility Compounds

For low volatility compounds, only the second term in equation (A-15) is significant. Then

$$k_v = \frac{H_c k_g}{LRT} \quad (A-20)$$

If the volatilization rate is gas phase mass transport resistance limited, a useful equation would have a form that would allow the ratio of the volatilization rate constant of the chemical to a second chemical found in the environment to be measured in the laboratory. The obvious choice of the second chemical is water. Thus, the water evaporation rate would be measured in the laboratory and used to estimate the volatilization rate constant in the environment, $(k_v^C)_{env}$, using the environmental rate for water evaporation. This concept is complicated by the fact that the rate of water evaporation is, for dilute solutions, a zero-order

^{*}This equation contains several approximations, which are discussed by Prausnitz (1969).

process because the concentration of water does not change during evaporation. Water evaporation rates are usually expressed in units of depth (length) time⁻¹, which is equivalent to units of flux, volume area⁻¹ time⁻¹.

The value of the gas phase mass transport coefficient for water, k_g^W , is calculated from the water evaporation rate or flux, N^W .^{*} For dilute aqueous solution, the equilibrium partial pressure of water above a solution, P^W , is expressed by Raoult's law (which, like Henry's law, cannot be derived from first principles),

$$P^W = P_s^W X^W \quad (A-21)$$

where P_s^W is the vapor pressure of water at the surface temperature, and X^W is the mole fraction of water, which approximately equals 1 for very dilute solutions. Then

$$C_g^W = \frac{P^W}{RT} \quad (A-22)$$

Also, for water $C_l = C_{sl}$; hence, mass transport of water is only gas phase limited. Then

$$N^W = k_g^W (C_{sg}^W - C_g^W) = k_g^W \left(\frac{P_s^W - P^W}{RT} \right) \quad (A-23)$$

Two-film theory assumes that the mass transport coefficient is

$$k_g = D_g / \delta_g \quad (A-24)$$

Then, the ratio of mass transport coefficients should be independent of the gas phase turbulence. Therefore, we suggest that

$$k_g^C / k_g^W = D_g^C / D_g^W = \text{constant} \quad (A-25)$$

* The superscripts C and W refer to the chemical and to water, respectively.

Then,

$$\left(\frac{k_g^C}{k_g^W} \right)_{\text{env}} = \left(\frac{k_g^C}{k_g^W} \right)_{\text{lab}} = \frac{D_g^C}{D_g^W} = \text{constant} \quad (\text{A-26})$$

Solving equation (A-20) for k_g , substituting into (A-26), and solving for $(k_v^C)_{\text{env}}$ gives

$$\left(\frac{k_v^C L RT}{H_c k_g^W} \right)_{\text{env}} = \left(\frac{k_v^C L RT}{H_c k_g^W} \right)_{\text{lab}} \quad (\text{A-27})$$

and

$$(k_v^C)_{\text{env}} = \left(\frac{k_v^C}{k_g^W} \right)_{\text{lab}} \frac{L_{\text{lab}} T_{\text{lab}}}{L_{\text{env}} T_{\text{env}}} (k_g^W)_{\text{env}} \quad (\text{A-28})$$

These equations suggest that the ratio should be constant and independent of turbulence in the gas phase (wind speed). Also the value of the ratio (k_v^C/k_g^W) can be estimated by calculating or measuring the diffusion coefficients or the ratio can be measured in the laboratory and be used to estimate $(k_v^C)_{\text{env}}$. We are not aware of any experimental data that support equation (A-28), but studies to verify the equation are currently in progress at the SRI laboratory.

Diffusion coefficients can be estimated using methods reviewed by Reid and Sherwood (1966). However, Liss and Slater (1974) have proposed that

$$\frac{k_g^1}{k_g^2} \approx \left(\frac{M^2}{M^1} \right)^{1/2} \quad (\text{A-29})$$

where M is the molecular weight of compounds 1 and 2. This equation is

a crude approximation that has little scientific basis,* but is adequate for preliminary estimates of k_g^1/k_g^2 . Then, solving (A-20) for k_g^C and substitution into the first term of equation (A-26), we obtain

$$\left(\frac{k_v^C}{k_g^W}\right)_{\text{env}} = \left(\frac{k_g^C}{k_g^W}\right)_{\text{lab}} \frac{H_C}{L_{\text{env}} RT_{\text{env}}} = \text{constant} \quad (\text{A-30})$$

and

$$(k_v^C)_{\text{env}} = \left(\frac{k_g^C}{k_g^W}\right)_{\text{lab}} \frac{H_C}{L_{\text{env}} RT_{\text{env}}} (k_g^W)_{\text{env}} \approx \left(\frac{H^W}{M^C}\right)^{1/2} \frac{H_C (k_g^W)_{\text{env}}}{L_{\text{env}} RT_{\text{env}}} \quad (\text{A-31})$$

Equation (A-31) can be used to estimate the volatilization rate constant of a low volatility compound. The value of $(k_g^W)_{\text{env}}$ must be estimated from field data. The water evaporation rate has been carefully measured for several lakes. The results are shown in Table A-1.

TABLE A-1. WATER EVAPORATION RATES FOR LAKES

Location	Average evaporation rate (cm sec ⁻¹ x 10 ⁶)	reference
Lake Hefner, Oklahoma	4.8	Marciano & Harbeck (1952)
Lake Mead, Arizona	6.8	Harbeck, et al. (1958)
Pretty Lake, Indiana	3.8	Ficke (1972)
Average	5.1	

Assuming that the average relative humidity is 50%, the average value of k_g^W for freshwater lakes is,

$$k_g^W = N_W RT / (P_g^W - P^W) \quad (\text{A-32})$$

$$= \frac{(5.1 \times 10^{-6})(62400)(293)(2)}{(18)(17.5)}$$

* This approximation would be correct if diffusion through the Knudsen layer, which is 1 to 2 mean free paths above the interface, determined the net evaporation flux. However, it can be shown that this diffusion is fast compared with both liquid and gas phase mass transport.

$$= 0.59 \text{ cm sec}^{-1}$$

$$= 2100 \text{ cm hr}^{-1}$$

The following procedure was used to estimate the lower limit of H_c that would cause the environmental half-life for volatilization of a low volatility compound to be less than three months. The half-life for volatilization of the chemical, $t_{1/2}$, can be calculated from

$$t_{1/2} = \ln 2 / (k_v^C)_{\text{env}} \quad (\text{A-33})$$

If the half-life is less than three months, $(k_v^C)_{\text{env}}$ must be greater than $9 \times 10^{-8} \text{ sec}^{-1}$. Substituting the following representative values into equation (A-31) and solving for H_c , we obtain

$$(k_v^C)_{\text{env}} > 9 \times 10^{-8} \text{ sec}^{-1}$$

$$M^C = 250$$

$$R = 62.4 \text{ torr liter mol}^{-1} \text{ K}^{-1}$$

$$L_{\text{env}} = 200 \text{ cm}$$

$$T = 20^\circ\text{C} = 293 \text{ K}$$

$$(k_g^W)_{\text{env}} = 2100 \text{ cm hr}^{-1} = 0.59 \text{ cm sec}^{-1}$$

$$H_c > \frac{(9 \times 10^{-8})(62.4)(293)(200)}{(18)(250)^{1/2}(0.59)}$$

$$> 2.1 \text{ torr M}^{-1}$$

Thus, if H_c is greater than about 2 torr M^{-1} , the environmental volatilization rate of the chemical may be less than three months.

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